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A CONCISE HISTORY OF CHEMISTRY

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A CONCISE HISTORY OF CHEMISTRY

BY

T. P. HILDITCH

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PREFACE

THIS book is an attempt to outline as briefly and succinctly as possible the historical development of chemistry, and is designed more especially for those students whose interest in this aspect of the science is stimulated by the inclusion of "Historical Chemistry" in the syllabus of examinations which concern them. It is therefore presumed that the reader is simultaneously acquiring, or already possesses, a fair knowledge of present-day chemical theory and practice, and, accordingly, no space is devoted to the actual explanation of hypotheses or reactions except in so far as the latter are directly bound up with the historical sequence of facts.

Whenever practicable, each section is arranged so that it follows approximately those lines upon which a student would learn the simple chemical facts in question; thus, the introductory chapters dealing with the older chemistry (down to Lavoisier) are succeeded by the history of elements and inorganic compounds, treated, as far as possible, according to the Periodic Law, whilst the details of other branches, such as organic and physical chemistry, follow in general the order given in the standard text-books. Many facts, important in themselves but not so germane to the general development of ideas, have been collected in tabular form for convenient reference, and the

book is concluded by a summary of the work of some notable chemists and a chronological survey of the experimental and theoretical advances in chemistry during the last two centuries. In order to secure a more compact volume, no detailed references have been given to the literature in which the discoveries, theories, etc., were published, but the dates given in all cases will assist the student to obtain the original account of any particular point desired.

I wish to acknowledge the kind help I have received from Dr. A. E. Dunstan, who read the book in manuscript; from Dr. S. Smiles, Dr. A. W. Stewart, and Mr. H. J. Page, who aided in the correction of proofs; and from Prof. J. N. Collie, F.R.S., who advised me with respect to the arrangement of certain parts of the work.

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A CONCISE HISTORY OF CHEMISTRY

CHAPTER I

THE EVOLUTION OF THE SCIENCE

§ 1. **The Chief Chemical Epochs**—History of any kind may be recorded in either of two ways :—

(1) Chronologically, as a whole;

(2) By taking one section of the subject at a time and treating each separate division chronologically.

The first alternative is usually employed in the case of, for example, a country or province, while the second would be necessary in dealing with a continent composed of a variety of races, each with its own life-story. We shall find it advisable to adopt this latter plan with regard to chemistry, for the science nowadays possesses so many branches and ramifications that it is very much easier to understand the evolution of the whole from a consideration of the development of the various individual parts. There are, nevertheless, certain well-marked epochs which should be noticed in the general progress of the science.

It is certain that no civilized race has yet existed in the world without giving some thought to the properties and mutual relations of the various sorts of terrestrial matter. Of course, no one can tell precisely where, when, and how chemistry really came into existence, and it would not suit our present purpose to discuss the matter at any length. Let it suffice to say that remote Chinese and Hindu philosophers appear to have paid attention to this branch of science, while our records

go back with certainty to the times of the ancient Egyptians and Greeks.[1] These devoted themselves to speculations about the ultimate composition of natural substances, and at the same time—notably in Egypt—the idea of the transmutation of metals began to develop. The predominance of this notion at about the commencement of the fourth century A.D. marks the close of the first or *Ancient Period*—the period of philosophic speculation—and the opening of the second, the *Alchemical Epoch*. This lasted for more than a thousand years, and it is said that even in the last century there yet existed individuals holding alchemical tenets; practically speaking, however, the ideals of chemists underwent a profound change towards the close of the seventeenth century. Alchemists were dominated by two pre-conceived and extraordinary ideas: firstly, that it was possible to change common metals into gold by a chemical process; secondly, that the change was to be accomplished by the agency of a substance, known variously as The Essence, The Philosopher's Stone, The Elixir of Life, etc., which possessed entirely supernatural powers.

The development of the physical sciences, on the other hand, had been uncommonly rapid during the seventeenth century, and this was largely due to the adoption of inductive methods. It is thus easy to see how chemists, tired of fruitless search on a vain quest, and sickened by the duplicity which was too frequently practised, turned to new methods. Robert Boyle in particular changed the trend of chemical reasoning, and thereby rendered his greatest service to science.

In the next period—the *Phlogistic Period*, dating from about 1700 to 1775—the properties of the most various bodies were examined with a view to classification. The property which attracted most attention was that of combustion—so much so that this era fittingly takes its name from the famous but incorrect theory designed to explain the phenomenon of burning.

[1] Berthelot's "Les Origines d'Alchemie" is a standard work for those wishing to study in detail the earliest era of the science.

In 1777 Lavoisier published his theory of combustion, worked out by the help of the balance, and made possible by Scheele's and Priestley's discoveries of oxygen; this inaugurated the era of modern chemistry, which may again be subdivided into three periods:—

(1) The *Fundamental Period*, comprising the labours of Davy, Dalton, Gay-Lussac, Berzelius, Dulong, Faraday, etc.

(2) The *Period of Static Structural Chemistry*, commencing with Wöhler's synthesis of urea in 1828, and comprising the foundations of systematic organic and physical chemistry.

(3) The *Period of Dynamic Structural Chemistry*, i.e. the development of the most recent views concerning the ultimate composition of matter, the structure of chemical (and particularly "organic") compounds, the nature of electrolysis, etc. This period may be said to have commenced about 1880.

We may, then, summarize the six periods of chemical history in the table on page 4, giving at the same time instances of familiar historical events which may serve in some measure to correlate the various dates.

§ 2. **The Origin of the Science and its Name**—There are various indications that some knowledge of the practical applications of chemistry existed long before the era of Western civilization. The Chinese, for instance, possessed means of manufacturing articles which in some cases cannot be made with the same degree of elegance at the present day; this implies a considerable acquaintance with some sort of technical chemistry. At a less indefinite date, which is still too remote to be fixed with any certainty, we find the Phœnicians and Egyptians well acquainted with the manufacture of glass and pottery; some of the simpler metallurgical processes were already practised, including the mechanical separation of gold, the smelting of iron, the preparation of mercury from cinnabar, and the separation of lead and silver. The arts of dyeing and embalming were also largely engaged in by the Egyptians. The Jews, too, in the

Period.		*Commenced.*		*Contemporary Events of the Period.*	
I.	Ancient	—	About 200 B.C.	Decline of Greek and rise of Roman philosophy.	
			47 B.C.	Fire at Alexandria.	
			216 A.D.	Sack of Alexandria by Caracallus.	
II.	Alchemical	(*a*) Transmutation about 300 A.D.	420	Withdrawal of Romans from Britain.	
			642	Alexandrian library burned by Arabs.	
		(*b*) Medicinal „ 1500 A.D.	About 1450	Renaissance of Learning.	
			1534-155 8	Reformation of Religion in England.	
III.	Phlogistic	„ 1700	1688	Downfall of Stuart dynasty.	
IV.	Modern	(*a*) Fundamental „ 1780	1789	French Revolution.	
V.	„	(*b*) Static Structural „ 1830	1827	Successful application of steam as motive power.	
VI.	„	(*c*) Dynamic Structural „ 1880			

reign of Solomon (and probably for some time prior to that period) recognized at least six distinct metals: gold, silver, iron, copper, tin, and lead.

Metallurgy at this early date was carried on chiefly in the northern part of Egypt; deposits of ores were fairly abundant in that region, and, in addition, the seaport of Alexandria afforded means for the import of ores from the various lands washed by the Mediterranean. Not infrequently metallic deposits, consisting of a mixture of metals or ores, would be found; sometimes much lead accompanied by a little silver, sometimes silver and gold together, sometimes other metallic mixtures. Moreover, methods were soon devised for preparing the "noble" from the "base" materials in such instances; what is more natural, then, than that the idea of the baser being transformed into the rarer metals should gradually come into the minds of these early metal-workers? Here is the origin of the transmutation theory; gold and silver were regarded, then as ever, as most precious and valuable; mixtures of these with common substances were found—perhaps Nature was slowly transforming the base into the rare? This suggestion developed into a most persistent and dominating belief in the alchemical period; and even now, centuries after the theory has been dropped, we retain in common use phrases which betray an innate leaning towards alchemical ideas, such as "base" and "noble" metals, "perfect" gases, etc.

The famous transmutation theory, then, probably arose from a very superficial kind of reasoning, and this may be due to the circumstance that the early metallurgists do not appear as a rule to have been in touch with the "philosophers" or learned theorists. The latter class of men, naturally most prominent in ancient Greece, had little in common with the former.

It is convenient to summarize at this point the chemica knowledge of the ancients:—

(1) *Practical.*—In China and India (?), in Phœnicia and Egypt: metallurgy, dyeing, glass, earthenware.

(2) *Theoretical.*—In Greece (500-200 B.C.) and Rome (100 B.C.-A.D. 150); vague, general observations on nature.

(3) *Experimental* (according to the modern meaning of the word).—Practically none.

With regard to the origin of the word "chemistry," there is a choice of about six very plausible "derivations," such as from the North Egyptian word "chemi" = Egypt; from χημεία = Egyptian art; from χημεία = black, etc. As these cannot all be correct, let us be content merely to say that the first use of the word "chemia" appears in an astrological treatise compiled by Julius Firmicus, a writer of the fourth century of the Christian era.

§ 3. **Alchemy: the Ennobling of Metals**—When we turn to review the next period of chemical history, it at first appears as if the Greeks had all the clear-sighted theories and the alchemists none, for the superabundance of views and metaphor are bewildering. There is a break of some 200 years between the latest philosophical writings and the earliest authentic alchemical works, and during this time a great change in view-point took place, culminating in the predominant belief in "transmutation," which appears as a well-known doctrine in all the latter treatises, although it is scarcely mentioned in the former. This is natural in view of the probable origin of the theory (p. 5) and of the fact that the old philosophy finally died out after Hypatia's murder, and was replaced by a system based on the Christian religion. The unscrupulous blending of Christian hypotheses and natural science led to as dismal consequences to both as the intolerance of Christian authorities to science has done in many an instance. Assuming that they possessed by revelation a divine "scheme" of the moral universe, the new race of thinkers extended it to the material world, and deduced that simplicity was the key-note and perfection the end of matter as well as of mind. Gold and silver were assumed the most perfect metals, "the end of Nature in regard to metals," and the original aim of alchemy was to "assist

Nature" by the application of certain agents or medicines, which, acting on the "baser" metals, should purge away the impurities and leave worthier members of the metallic state. Much later the idea arose that such agents—especially the greatest of all, the Philosopher's Stone, Alkahest, Elixir, etc.—ought to be of service to men's as well as metals' ills; and iatro-chemistry, in which chemistry is looked upon as the servant of medicine, was developed. This branch of alchemy, and the alchemical theories of the ultimate constitution of matter, are discussed later (pp. 9, 28).

Because of the universal desire for gold and silver, and the ease of making alloys or amalgams bearing strong superficial resemblance thereto, the aim which alchemists set before them, albeit at first purely philosophical, naturally lent itself to deception, and alchemy quickly became degraded into a mere gold-imitating art. Various popes and princes therefore proscribed its practice in their realms, but usually found it too valuable a means of filling empty purses to be very severe on its adepts. Consequently nearly every European court had its private alchemist, who in general was merely a swindler, not a scientist, with whom matters went hard in case of detection, but who usually found it sufficiently easy to secure against such a contingency and to make a comfortable living. For a long while, indeed, true chemists were few and far between, till better ideals once more arose, thanks in the main to the outspoken utterances of Boyle, Kunkel, and others. With the charlatans we are not concerned, but proceed to summarize as far as we can the general trend of theory—a difficult task, since, to a greater extent than at any other period, each followed his own independent path.

Nearly all alchemical writers refer to one Hermes Trismegistus as the father or originator of alchemy. This somewhat mythical person was supposed to have developed very largely the practical side of alchemy in Egypt at an indefinitely remote period; his existence (except in the minds of these writers) is a

matter of doubt, but his name has certainly survived, even in the chemical parlance of the present day. It is amusing to note how, later on, devotees of the "hermetic art" in their anxiety to invest their science with a touch of religious sanctity asserted that the first of their cult were Biblical characters, such as Adam, Tubal-Cain ("an instructor of every artificer in brass and iron"), Moses and Miriam, or Job ("Thou shalt lay up gold as dust")! In reality the science of alchemy was chiefly fostered in the museum of Alexandria [1] in the first centuries of our era, under both heathen and Christian teachers, as Zosimos of Panopolis (*circa* A.D. 420-450) and Bishop Synesius (*circa* A.D. 400) until the decay of the Western Roman Empire and the advent of the Arabs, i.e. until about A.D. 640. The Arabs took up science with wonderful zeal, for within a century universities, which soon became famed for mathematics, medicine, astronomy, and alchemy, began to spring up in Bagdad, Cordova, Seville, Toledo, and elsewhere, and to these in the course of the next four centuries came many Western European students. Geber is the first alchemist of note whose existence is authentic, and of his actual life we know very little, except that he was an Arab physician, whose reputation lasted down through the Middle Ages. No other Mohammedan alchemist attained such fame as he, and he wrote several works on chemistry, which still exist in the form of Latin translations. When Arab learning declined (about 1200) alchemy was propagated in England, France, and Germany by the students mentioned above, and indeed was fully developed in Western Europe by the year 1400. It was

[1] The "Alexandrian Academy" was founded as a school and library by Ptolemy Soter, destroyed by fire in 47 B.C. and A.D. 216, and taken by the Arabs in 642. It is interesting because (1) it must have acted as a point of contact for Greek theorists and Egyptian metal-workers, (2) it was the final seat of the old heathen philosophy, and although the Christian authorities murdered the latest of the philosophers, Hypatia, in their jealous endeavours to stamp it out, enough of their writings must have been left to enable the Arabs, some two hundred years later, to assimilate and propagate science as known to Hypatia, and her disciples.

carried on notably in "apothecaries' shops," which, designed for the purpose of preparing the simple medicines then used, served also to train numbers of keen alchemists.

The fact that chemistry in the Middle Ages was dominated by mediæval religion will account for many of the biassed, prejudiced ideas which held sway, and the influence of the desire to make gold and the belief in the possibility of transmutation all helped to enshroud the real end of the science in a mist of preconceived notions and a tangle of hopeless beliefs. Yet it must not be supposed that this period of chemistry was unfruitful. Indeed it has been very well said that the hunt for the Philosopher's Stone and unlimited gold resembled very much the search of the sons of the man who said on his deathbed that there was a fortune buried in his vineyard—and we, the descendants of the alchemists, are still reaping the benefit from the fertile discoveries these made in the course of so much misdirected ploughing.

§ 4. **Alchemy: Medicinal**—While the philosopher's mind was fixed on one theme—gold manufacture—his experiments were naturally concerned only with metallic derivatives, so that few of the new facts discovered related to any but this class of compounds. When the Renaissance of learning and the Reformation led to a wider intellectual outlook the scope of chemists' views also appeared to broaden, and a larger field of use for chemistry was opened up. Originally the doctrine of the ennobling of metals had been deduced by analogy (however fanciful) with human moral development, and now, conversely, the beliefs (for theories were to alchemists "articles of faith") which had arisen as to the composition of metals were applied to the healing of physical disease. Basil Valentine and a few other workers of the first alchemical period here and there applied isolated metallic preparations as medicinal remedies, but Paracelsus (sixteenth century) was the first to emphasize the close inter-dependence and alliance of chemistry and medicine. He assumed that the three "principles," sulphur, salt, and

mercury, which were held to constitute the different metals, also composed the human body, and that illness was the result of deficiency or excess of one or more of these in the organism —an assumption which was characteristically accepted as a creed by Sylvius, van Helmont, Tachenius and other alchemists of the next few generations. The "medicine of the third order," the Philosopher's Stone, which should bring perfection to weak and erring metals, was naturally supposed to perform the same function for mortals, endowing them with an indefinite span of life and resistance to all physical decay. This fusion of medicine and chemistry was of advantage to both, but particularly to the latter, which then attracted men of wider culture than previously; it led to the discovery, too, of further new facts and compounds, especially in the domain of what is now "organic" chemistry, and unintentionally paved the way for the emancipation of chemistry from a gold-making art to a truth-seeking science.

At the present day there exist in nearly all civilized countries societies for the extension of chemical science and numerous periodicals devoted to the same purpose; but in alchemical times there was nothing of this kind, and the isolated character of each individual's work is very conspicuous. (Cf. Appendix, pp. 209, 210.)

In the earlier history of alchemy this independence was due to the selfish, competitive motives aroused by the quest for gold and the Philosopher's Stone. Later on the change to iatro-chemical ideals, which postulated health for all rather than wealth for one, and the repeated failures to obtain the "elixir," which aroused a feeling that united work might solve problems which baffled isolated workers, caused the formation of various alchemical unions. These were chiefly "secret societies," and they thrived from about the beginning of the seventeenth to the middle of the eighteenth century, but were in no way comparable to or connected with the real scientific societies then existing, such as the Royal Society of London (founded 1663).

Alchemy consisted, then, in the later stages of its existence, of two branches, the one concerned merely with gold manufacture, the other with the application of chemistry to healing. The latter side of the subject cannot be said to have been abandoned, but rather to have been extended by the rapid adoption of the inductive method of research, its development in one direction (the phenomena of combustion) leading to the doctrine of phlogiston, which characterized the next period of chemical history. The efforts to make gold from baser metals were so unsuccessful, and yet afforded such scope for duplicity and charlatanism, that a great deal of scepticism arose in course of time as to the possibility of metal-transmutation at all, and gradually the idea died out. It might be pointed out that, until definite proof was given for regarding the metals as elements (i.e. in Lavoisier's time), it was not chemically wrong to believe in the possibility of changing one into another.

§ 5. **The Beginnings of Modern Inductive and Experimental Method**—One of the first to apply the "inductive" method to chemistry was Roger Bacon (thirteenth century); then, towards the end of the seventeenth century, the necessity of putting aside the subsidiary aims which chemistry might serve seems to have been more widely felt, and the efforts of chemists were directed along new lines, notably by the work of Boyle and Kunkel. The latter, himself an enthusiastic alchemist, was concerned more particularly with the careless phraseology and frequent duplicity of his contemporaries, and denounced both with considerable vigour. Boyle's writings, however, show that he had little faith in alchemy, but possessed views on the nature of chemical combination and of chemical elements which have stood their ground; moreover —and this is very noteworthy—he stated that experimental methods and careful observation were the only sure paths to development. The general adoption of these views, although hampered for a time by neglect of quantitative investigation, has undoubtedly been the cause of the rapid progress of the science to its present position.

Let us contrast, then, the three different methods of investigation which we have now discussed.

The ancients based their theories on careful observation of natural phenomena, but made no experiments to shed further light on their assumptions.

The alchemists based their theory on one fundamental assumption (the simplicity and unity of nature), and made many experiments to show that the theory was certainly true.

The modern inductive method, which chemists owe especially to Boyle, is to base a theory on a consideration of the known facts, thence to design new experiments to throw fresh light on the subject, and, from the new facts so discovered, to modify or confirm the original theory, and then repeat the process indefinitely.

The whole difference of the systems lies in the different relations which the various ages assigned to the bearing of experiment and observation on theory.

§ 6. **Chemistry in the Phlogistic Period**—It has been necessary to give a detailed account of the chemistry of the alchemists and ancients, because their view-points differed fundamentally from those of all later investigators. Chemistry, indeed, as understood at present, originated when alchemy decayed and the attainment of chemical truth was made the goal of the science. The phlogistic chemists form a kind of link between old and modern workers, for they aimed at the extension of chemical knowledge, while their theories and methods were often not far in advance of those of their predecessors, the alchemists. We will therefore conclude this sketch of chemical evolution by a résumé of the work done by the phlogistonists, and then pass on to the history of the various branches of chemistry.

In the phlogistic period we notice first of all that qualitative investigation was the almost invariable rule—the use of the balance being quite exceptional. The chief subject of experiment was the phenomenon of combustion, usually explained

at that time on the "phlogiston" hypothesis (cf. chap. ii., p. 15).

Much progress was also made with methods of qualitative analysis, and during this epoch the composition of water (Cavendish) and of air (Mayow, Priestley, Scheele, etc.) was cleared up. In consequence of the manipulative processes introduced by Boyle and (in lesser degree) the later iatro-chemists, the investigation of gases went on rapidly and the isolation of nitrogen or "phlogisticated air" (Rutherford, Scheele, Priestley), oxygen or "dephlogisticated air" (Scheele, Priestley), carbon dioxide or "fixed air" (Black), hydrogen (Cavendish), and chlorine (Scheele) among other gases may be placed to the credit of the "phlogistic" chemists. The mutual relationship of salts, acids and bases was also recognized, Rouelle (1744) defining the former as a combination of the two latter, and also distinguishing between neutral, acidic, and basic salts. The more ordinary acids became fairly well-known, sulphuric, phosphoric, nitric and hydrochloric acids being classified as "mineral acids," while formic, citric, oxalic, uric, tartaric and others were termed "animal acids"; bases such as the alkalies and alkaline carbonates, and "earths" such as the calces of magnesia alba, alum, barytes, quartz, etc., were also characterized at about this time. In what is now called organic chemistry, the preparation of alcohol, wood spirit and various "ethers" was advanced, while Scheele, who discovered most of the "animal acids" just mentioned, also isolated glycerine from fats.

Technical chemistry now rose to be an independent branch of the science, the following being the more notable developments of the period: the manufacture of nitric, sulphuric, and Nordhausen sulphuric acid; the metallurgy of zinc, and processes for gilding and silvering metals; the fabrication of porcelain (Sèvres); and of mineral dyes and paints, such as Prussian blue ($Fe_4^{III}[Fe^{II}(CN)_6]_3$) and Scheele's green.

CHAPTER II

THE CHEMICAL HISTORY OF FIRE, AIR, AND WATER

§ 1. **Fire and the "Fire Principle"**—Of the four "Aristotelian elements" it may be said that, while chemists always have been and will be concerned with the constituents of earth, the nature of fire, air, and water was practically cleared up in the course of a century, or, more precisely, during the phlogistic period. It is thus convenient to study these three together at this point. It was the universal custom of the ancient philosophers to consider all three as elements, but it must be remembered that "element" at that period meant rather a fundamental property, than a fundamental unitary kind of matter. Later on, some of the alchemists held that by interaction of pairs of these four elementary properties, three fundamental principles, akin to mercury, sulphur, and salt, were formed. It is easy to see why "fire" was given a position equal to the other three elements, for while the gaseous, liquid, and solid states could be represented fundamentally by air, water, and earth, the equally patent state of "flame" was supposed to be the manifestation of the principle of "fire".

The earlier alchemists did not turn their attention very seriously to the problem of combustion, but in the iatro-chemical era, Sylvius (*circa* 1650) suggested that sulphur (the alchemical "principle") was the principle of fire, and also drew attention to the analogy between burning and breathing. This suggestion was accepted by other alchemists, such as Homberg and Kunkel; Boyle, who, to use the title of one of his works, was more of

a "sceptical chymist," regarded it as possible, but not proved, and preferred merely to call the fire principle a "combustible earth".

In the meantime Mayow (1668-9) showed that there was a substance in air which took part both in the calcination of metals and in respiration, but did not seemingly pursue the subject far enough to give a complete explanation. At about the same date the alchemist Becher was trying to revive the old "principles" under new names, "mercurial, vitreous, and combustible earths"; the latter, "terra pinguis," was set free when combustion or calcination took place. Unfortunately, as has frequently happened, preconceived assumption met with more notice than precise observation (due in this case to Mayow), and Stahl, one of Becher's pupils, elaborated Becher's idea into the famous phlogiston theory.

Stahl assumed that all combustible or calcinable matter contained a substance "*phlogiston*"[1] which was evolved during the process of burning; the more readily and completely combustible the substance, then, the greater was the amount of phlogiston it contained. Coal was supposed to be particularly rich in phlogiston, for on heating it is almost entirely burnt away, while by heating it with many metal oxides the metal is reformed. On the other hand, the metals, etc., were supposed to be the products of union of phlogiston with the metal calces, and we can represent these views by an equation, perhaps, as follows :—

$$\text{Metal} \rightleftarrows \text{Phlogiston} + \text{metal calx (oxide)}.$$
$$\text{Sulphur} \rightleftarrows \text{Phlogiston} + \text{sulphuric acid}.$$
$$\text{Phosphorus} \rightleftarrows \text{Phlogiston} + \text{phosphoric acid}.$$

When a calx or sulphuric or phosphoric acid is heated with matter rich in phlogiston (coal), the metal or sulphur or phosphorus is "revived". This idea is a direct inversion, so to speak, of our modern view of combustion, for we hold that

[1] Some consider that "phlogiston" has been in a manner realized in the form of the "heat of formation or decomposition" of a body.

addition of oxygen takes place in combustion, and elimination of oxygen in reduction. In order to make the relation of phlogistic to modern views quite clear, we may add that:—

Elimination of phlogiston = oxidation (combustion).
Addition of phlogiston = reduction (elimination of oxygen).

Stahl suggested that a similar explanation, based on phlogiston, could be found for respiration, which would thus consist of an exhalation of phlogiston.

This theory gave a concise explanation of a large number of miscellaneous facts, and it was exceedingly simple. Unfortunately, it was also hopelessly impossible; the "elimination of phlogiston" was invariably accompanied by gain in weight, and conversely! This did not deter the earlier adherents of the theory, at all events, from accepting it as blindly as did the alchemists the doctrines of metal transmutation and the existence of the elixir of life. One cannot quite understand the attitude of chemists who said that "although" gain in weight always accompanied combustion, and loss in weight what we now call reduction, yet "notwithstanding this" the former phenomenon was due to loss, and the latter to gain, of phlogiston. Of course little attention was paid at that time to quantitative methods, and the importance of mass as the only reliable guide to the "amount of matter in a substance" was unrealized; but even much later, phlogistonists suggested, as a way out of the difficulty, that their fire-stuff possessed a negative weight.

That the phlogistic theory was in no wise a worthless attempt at an explanation of combustion is proved by the number of useful discoveries made in all departments of chemistry in the eighteenth century and by the men whose allegiance to it did not prevent them from being brilliant chemists (Black, Cavendish, Priestley, Scheele, Bergman, etc.). The nature of air and water, indeed, was finally elucidated during this epoch, and it will be most convenient to deal with these before proceeding to give a description of the advent of Lavoisier and the decline of phlogiston.

§ 2. **Air: a Mixture of Gases**—For long ages people

were content with the old notion that air was an "element," a simple substance, but in course of time two circumstances combined to render this view open to question.

(1) Van Helmont, whom many regard as the "founder of pneumatic chemistry," showed that it was possible to isolate gases from various materials, and that these gases frequently possessed varying properties. He, indeed, was the first to use the term "gas" (*geist* = spirit), and differentiated "gases," which he supposed to be unliquefiable, from "vapours," or gases which on cooling condensed to the liquid state. He seems to have isolated carbonic acid in various ways (combustion, fermentation, etc.), and gave specific names to a number of other gases, but we cannot tell in many cases to which particular substance he refers.

(2) A little later (1650-90) the behaviour of substances heated in an enclosed volume of air began to be observed; Mayow (1668-9) noted that when metals were calcined or animals breathed, a part of the air (the "*spiritus nitro-æreus*," also a constituent of saltpetre) was used up, while the remainder ("*nitrous air*") was somewhat lighter than the original air, was insoluble in water and did not support combustion. Similarly Boyle's work on calcination and respiration showed him that air was a mixture and that only one part of it was actually essential to burning or breathing, but neither he nor Mayow definitely prepared this active ingredient.

The fact that air itself is ponderable was first proved by Rey (1630). These facts comprise practically the whole knowledge of air down to the middle of the eighteenth century. The phlogistonists regarded it simply as a receptacle into which phlogiston escaped in cases of combustion, etc., and if it was desired to explain the incapability of some gases to support life or flame, did so by the assumption that such were already "phlogisticated,"—saturated with phlogiston. Little material progress was made till later upholders of the phlogistic theory (Black, Priestley, Scheele, etc.) devised means for separating,

collecting, and manipulating gases which rendered their more minute investigation possible. Priestley, for instance, introduced the familiar "pneumatic trough" and "beehive shelf" and also utilized mercury, instead of water, as the collecting medium. We may thus say that at about 1750 air was believed to be a mixture of at any rate two ingredients, one which supported life and one which did not, or was a gas "partly saturated with phlogiston".

§ 3. **Air: its Constituents**—The bulk of the work of the later phlogistonists on air was of a qualitative nature, but exceptions are to be noticed in the case of Joseph Black's work on carbonic acid (1750-5) and Cavendish's analysis of air and water (1785 onwards). The crucial point of the problem was reached when Scheele and Priestley simultaneously and independently discovered *oxygen* in the summer of 1774. Both of these were examining the gases evolved from the "calces" of metals under different conditions, and both obtained oxygen by heating red oxide of mercury, and noted that it supported combustion similarly to air, only very much more vigorously. Their adherence to the phlogiston theory prevented them from arriving at the correct explanation of combustion, but they recognized that air was a mixture of two different gases. Scheele also obtained the new gas by heating saltpetre alone, and by warming black oxide of manganese with phosphoric or sulphuric acids; he called it *fire air*. Priestley obtained it from minium (Pb_3O_4) as well as from mercuric oxide, and named it *dephlogisticated air*, from the readiness with which it "absorbed phlogiston". By finding an absorbent for the new gas (Priestley (1775) used "saltpetre gas," nitric oxide, and Scheele (1777) ferrous hydrate or phosphorus) both proceeded to isolate the other constituent of air in a tolerably pure state, and found it to be somewhat lighter than air and a non-supporter of combustion, thus confirming Mayow's previous work (p. 15); it should be noted that the existence of oxygen itself was practically discovered by Mayow and by Boyle, although neither succeeded

in its isolation. This inactive part of the air, which Priestley termed *phlogisticated air*, and Scheele *spent air*, had also been isolated a little earlier (1772) by Rutherford, who adhered to Mayow's name, *nitrous air*. A number of other scientists also worked on this gas at about this period, and it acquired a variety of names. Fourcroy in 1788 and Berthollet in 1791 showed it was a constituent of animal tissues, and the former author, from its relation to the "alkaline" ammonia, suggested the name *alcaligène ;* Lavoisier used the term *mephitic air* and later *azote* —a name which means the same as the German *Stickstoff* (suffocating substance). Its modern name, *nitrogen*, was first used by Chaptal, on account of its relation to nitre. It should be noted that the elementary character of the gas was not realized at this time, nor indeed for a considerable period after, for Davy and Berzelius believed it to be made up of oxygen and another element—a view which was not finally abandoned till about 1820.

We must now consider the other constituents of air—carbonic acid, water, and the "rare gases of the atmosphere".

The presence of *carbonic acid* was appreciated even before Mayow's time, for van Helmont (early part of the seventeenth century) noticed its occurrence in air, in caves, in mineral springs, and in animal organs, and showed how to prepare it by burning coal, fermenting wine or decomposing chalk or "potashes" with vinegar. He called it *gas sylvestre*, but confused it with other gases which do not support combustion. Black (1750-5) also realized its presence, and called it fixed air, but we must discuss his work somewhat later, as it is concerned with the composition of the alkalies and alkaline carbonates rather than with that of air. Lavoisier (1775-6) and Dalton (1803) both determined with more or less accuracy the proportions of carbon and oxygen present in the gas, but this we can also deal with more appropriately in a later chapter. We should mention, however, that Scheele and Priestley each showed that when a candle burns in an enclosed air-space, exactly as much *fixed air* is generated as *dephlogisticated air* is consumed.

It has already been said that Cavendish was one of the few chemists of the phlogistic period who concerned themselves with quantitative research, and as a matter of fact, he made some exceedingly accurate analyses of air, showing that its composition was practically constant, but varied within very small limits. He estimated the oxygen by explosion with hydrogen, and then to see if the residual *phlogisticated air* was homogeneous, sparked it with excess of oxygen till no further contraction took place. He stated (1785) that "if there is any part of the phlogisticated air of our atmosphere . . . which differs from the rest . . . we may safely conclude that it is not more than $\frac{1}{120}$ part of the whole". A hundred and ten years later it was proved by Lord Rayleigh and Professor Ramsay that a little less than one per cent of the atmosphere was made up of a series of "inactive," chemically inert, gases. We will summarize the knowledge of air gained by the end of the phlogistic period and then return to the description of these "new" gases:—

PERIOD: *Ancient, Alchemical.* — PHLOGISTIC.

AIR → An element → A mixture of gases (Mayow, Boyle).

Modern Name.	*Definitely Isolated.*	*Phlogistic Names.*	*Regarded as—*
Oxygen	1774	Fire air (Scheele) Dephlogisticated air (Priestley) Spiritus nitro-æreus (Mayow)	Air devoid of phlogiston.
Nitrogen	1772	Spent air (Scheele) Phlogisticated air (Priestley) Nitrous air (Mayow) Mephitic air, Azote (Lavoisier) Nitrogen (Chaptal), etc.	Air saturated with phlogiston (Priestley), or Nitric acid saturated with phlogiston (Cavendish).
Carbonic acid	About 1620 or earlier	Gas sylvestre (van Helmont) Fixed air (Black)	Various, e.g. Phlogisticated muriatic, nitric, or sulphuric acid.
Water	—	—	An element.

§ 4. **Air: its "Inactive" Constituents**—The history of the five "inactive gases of the atmosphere" is comprised within a very recent period—the last fifteen years; and much of the work of their discovery, curiously enough, was carried out within a few hundred yards of the house in Gower Street, London, in which Cavendish, the last previous worker on the subject, lived a century before. The isolation of *argon*, the first of the series to be recognized and also the most abundantly occurring member, was due in the first instance to physical research, Lord Rayleigh (1893), who was engaged in checking the densities of the principal gases, observing that nitrogen from the atmosphere was always slightly heavier than that prepared from chemical compounds. He and Ramsay found this was not due to any peculiarity of the *nitrogen* present in either case, and therefore set out to repeat Cavendish's work on the question of the homogeneity of nitrogen—only with all the advantages of modern appliances and methods. The meaning of the last sentence may be realized when it is reflected that these later investigators had at their command (*a*) spectrum analysis, whereby traces of any gas could be qualitatively determined with the greatest ease (cf. chap. x., p. 186); (*b*) methods for cooling air sufficiently to liquefy it, whereby huge volumes of gas could be treated at once (cf. chap. x., p. 174); (*c*) chemical means of absorbing nitrogen and other gases which were unknown in Cavendish's time. They found, by repeating Cavendish's experiment of sparking the residual gas with oxygen over potash, and also by passing nitrogen repeatedly over heated magnesium or calcium, that a residue of inert gas, giving an altogether new spectrum, was left. This they termed *argon*, from its incapability of entering into chemical reactions.

It was known that a gas, supposed to be nitrogen, was often found occluded in uranium minerals (clèveite, bröggerite, pitch-blende, etc.). These were next examined by Ramsay and from them in 1895 he obtained another inactive gas much lighter than argon, previously only observed in the sun (by Sir N.

Lockyer, who christened it *helium*, in 1868), and at once recognized by its spectrum (with a notable yellow line—"D_3"). Argon was also sometimes obtained, one mineral—malacone—giving this as the chief occluded gas. The residue from air termed "argon" was therefore prepared in large amount in 1898 by Ramsay and Travers and fractionally distilled at very low temperatures; two main fractions were obtained, and of these, the lower boiling one gave by repeated distillation two gases, helium and another new member, *neon*, while the other consisted mainly of pure *argon* with two heavier gases, *krypton* and *xenon*. There was thus obtained a series of five new gases of unprecedented nature, in that they seemed to be devoid of all chemical affinity, no compound of any of them being known. Their physical constants have been determined fairly fully and are given in the table below; the atomic weights are determined from the densities, for Ramsay found by the method of Kundt and Warburg (cf. p. 189), that the ratio of specific heat at constant pressure to that at constant volume was about 1·60 in all cases, the gases being accordingly monatomic. The spectra, boiling-points, melting-points, etc., have also been determined by various workers, notably Ramsay, Travers, and Dewar; helium was not liquefied for some time, but Kamerlingh Onnes finally succeeded in condensing it by the Linde-Hampson process (p. 174), in 1908. Careful search has been made by Moore in Ramsay's laboratory for members of the series heavier than xenon, but without success (1908). The table shows, as well as the physical properties, the approximate amounts of each present in air, from which it will be seen that the designation "rare gases of the atmosphere" is not very apt, since together they comprise almost one per cent thereof, besides occurring occluded in various minerals, and dissolved in many springs, etc. Their relation to the problem of radio-activity is not yet completely understood, but it may be said here that Ramsay has proved that helium at least is one of the disintegration products of radium, and that "radium emanation" is a gas possessing the properties of a higher member of the series.

Name.	*Percentage in Atmosphere.*	*Atomic Weight* (1910).	*Boiling-point* (760 m.).	*Melting-point.*
Helium	0·0005	4·0	4·5° abs.	Below 3° abs.
Neon	0·0025	20·0	− 243° C.	− 253° C.
Argon	0·942	39·9	− 186·1° C.	− 189·6° C.
Krypton	0·00002	83·0	− 151·7	− 169·0
Xenon	Less than any of the above	130·7	− 109·1	− 140·0

§ 5. **Water**—The story of water is a much simpler one than those of either air or fire. From the earliest times right down to the end of the phlogistic period (and, in isolated instances, even later) it was looked upon as an "element". The ancients seem to have thought that water and air could be transformed into each other, and also that water was readily converted into "earth"—another proof that "element" did not then mean a definite unitary species of matter. The latter idea crops up persistently through the next two periods: thus Basil Valentine, who realized the importance of water to plant and animal life, held that it was transformed in the organic economy into earthy matters, and amongst the phlogistonists we find Scheele engaged in a qualitative analysis of the solids left by evaporation of water (he mentions lime and silica as the chief), while Lavoisier's first purely chemical service was to show that such solids were either primarily dissolved in the water, or dissolved by it out of the containing vessels.

We owe the discovery of the compound nature and qualitative composition of this all-important liquid, however, to Cavendish, who proved definitely that when *hydrogen* burns, water is the sole product of combustion. And here we may conveniently recount the history of *hydrogen*. The gas and its formation from iron and dilute acids were known to van Helmont, who seemed to confound it with carbonic acid. Its inflammability had been observed by others of the later alchemists and by Boyle; its reducing properties caused not a few of the phlogistic chemists to look upon it as *phlogiston* itself. The liquid formed when it burned was usually believed to be

an acid until, as just mentioned, Cavendish (about 1782) showed this to be pure water. He proved that hydrogen (or *inflammable air*, to use his phlogistic term) was only explosive in presence of air or oxygen, thereby pointing out the remaining constituent of water, and he determined the relative weight of the gas with moderate accuracy. Although Cavendish used hydrogen in determining the composition of air, it was Lavoisier who, in 1783, made the first quantitative synthesis of water. Lavoisier (1787) also gave hydrogen its modern name ("water-producer"), and showed how this gas could be formed by the action of steam on red-hot iron. The direct quantitative analysis of water came a little later, when Nicholson and Carlisle succeeded in decomposing it by electrolysis (1800). The true composition of water, then, became known at about the beginning of the nineteenth century, but the notion of its elementary nature died very hard, even Priestley remaining unconvinced for some years.

§ 6. **Fire: Lavoisier's Revolution**—In following up the history of air and water we have been forced to make a digression from that of combustion, which it will be recalled had been traced down to the time at which the phlogistic theory held full sway. We must now return in point of time to the years immediately preceding and following the French Revolution (1791)—as crucial a period for modern chemistry as for modern politics, though for vastly different reasons.

Somewhat previous to the year 1770 the French scientist Lavoisier was attracted by the twin phenomena of combustion and calcination, owing, in the first instance, to a request to investigate means for lighting the streets of Paris. As a physicist (and physics at that time meant mainly astronomy, optics and mathematics—all three sciences requiring precision of measurement) it was natural that he should have paid much more than usual attention to the *quantity* of the substances reacting, and that to this end he should have provided himself with a delicate balance. In 1772, in a private communication

to the French Academie des Sciences, he reported that metals, phosphorus and sulphur gain in weight and absorb "air" when heated in the atmosphere, while by heating a metal oxide (litharge) with coal much "air" was generated, as well as the reduced metal. This report betrays a tendency to go to the opposite extreme of the usual failing, or, in other words, to neglect the *qualitative* side of chemical reactions, for he failed almost entirely to distinguish between the different kinds of "air". Let it be remarked, too, that increase in weight on calcination had been observed by Rey and Mayow more than a century previous to this, the latter being apparently well on the way to the correct explanation of the process when, at a somewhat early age, he died.

Lavoisier, however, repeated the work of 1772 and produced a series of results which settled once and for all the problems of combustion, calcination, and respiration. These must be briefly summarized.

In 1774 he heated tin in a closed vessel and found the weight to be exactly the same before and after the process; but on opening the vessel air entered into it in an amount which showed that the deficit of air in the vessel was equal to an increase in weight which the tin itself was found to have undergone. During the same year Priestley told him of the isolation of "dephlogisticated air". Lavoisier then repeated the tin experiment with mercury, and from the oxide formed he reproduced the new gas according to Priestley's method; in this way he realized that the essential part in these processes was played by "dephlogisticated air"—it is unfortunate to have to say that he avoids any mention of either Priestley or Scheele's work on the discovery of that gas! The next two years were occupied by proving that the combustion product of diamond and of wood charcoal was "fixed air," and that many "organic" bodies (alcohol, oils, fats, etc.) gave only fixed air and water by their combustion; this, of course, showed such bodies to be made up only of carbon, hydrogen (and perhaps oxygen), but

the composition of water not being then known, this deduction was not made for some few years. In 1777 he showed that phosphorus leaves four-fifths of the volume of enclosed air in which it burns untouched, but completely consumes similarly enclosed dephlogisticated air; that sulphuric acid consists of sulphurous acid (known to be formed when sulphur burns in air) and dephlogisticated air, by prolonged heating of quicksilver with sulphuric acid, when first the former and then the latter gas is evolved (this experiment, in separate parts, had been made previously by Priestley); and that nitric acid is similarly constituted (the more detailed investigation of the composition of nitric acid is due to Cavendish). With all these facts, he was in a position to enunciate his "*oxidation theory*": *Substances burn only in "pure air," which is used up in the process, the weight of air used balancing the gain in weight of the substance. The product of combustion is usually an acid, but metals give the metallic calces.* A little later, concluding that his "pure air" was a constituent of all acids, he suggested its modern name, *oxygen* (1781). This later work consisted in investigating the combinations of metals with oxygen and the nature of the different "calces". The only difficulty in the way of his theory was that no explanation was given of the reasons for the dissolution of metals in acids and the evolution of hydrogen at the same time. Cavendish's synthesis of water (1783) gave the clue to this, and so it may be said that by about 1785 Lavoisier's "oxidation theory" was complete, and in the course of the next two decades completely supplanted the topsy-turvy explanation furnished by the phlogistonists.

CHAPTER III

THE ULTIMATE CONSTITUTION OF MATTER

§ 1. **Ancient and Alchemical Views**—In the sixth century B.C. Thales, Anaximenes and Heraclitus assumed for varying reasons that water, air, or fire respectively was the primary material out of which the universe was evolved. Such views were not of great individual influence, but Empedocles, about 440 B.C., gave utterance to the idea of *four* fundamental elements—earth, air, fire, and water—a view possibly derived in some degree from dimly-known Hindu and Chinese systems of thought. Some hundred years later Aristotle modified this theory by teaching that "matter" was the outward result of the combination of "properties"; there were four essential "properties"—heat, cold, damp, dryness—besides a number of secondary ones, all carried about by one original matter. Combinations of these properties, two by two, were the "elements" from which all matter was made; thus:—

Properties.	*Element.*	*Properties.*	*Element.*
Heat + damp	AIR	Cold + damp	WATER
Heat + dryness	FIRE	Cold + dryness	EARTH

He further declared that another element of an immaterial or ethereal nature was necessary for a complete explanation of natural phenomena (this ethereal constituent was later called the "quinta essentia," and long after this was sought by the alchemists as the "purest" form of matter, and identified by them with their imaginary elixir). Aristotle's somewhat fanciful doctrine is noteworthy, because by the mutation of his

"properties" the observed transformations of natural bodies could be explained.

Somewhat earlier (about 425 B.C.) Democritus had suggested that by repeated subdivision of matter a point would be reached when no further subdivision was possible. The body thus isolated—a "first beginning," or atom of matter—was the ground material of the universe, and, according to our philosopher, all such atoms were of the same nature and in continual motion, but differed in form and size.

These two doctrines were co-ordinated and developed by succeeding philosophers, notably by Epicurus (345-274 B.C.), and an elaborate account of the latest phase of ancient theory is given by the Latin poet Lucretius in his work, "De Rerum Natura," published about 58 B.C. "The void, or æther, pervades everywhere, while the matter is made up of a certain primal element and its aggregates. This element exists in the form of infinitely small, ever-vibrating first-beginnings or atoms, of finite shape, but giving rise by varied combinations to bodies of infinite shape, either solid (when the atoms are tightly packed) or liquid or gas, air or light (when they are not in such dense aggregates)."

The term element possessed an indefinite meaning in the next period, and sometimes referred to the actual matter in a substance, sometimes to a property of that matter, but never to a simple substance! In general, the alchemical "element" meant something more related to properties than to matter itself—something which we can perhaps best depict by the word "principle". Thus Geber (eighth century) states (it is not clear upon what grounds) that all metals contain two such principles—sulphur and mercury, the latter imparting metallic properties, such as glance, ductility, etc., and the former readiness of decomposition, the different properties of metals depending on the varying amounts of these two principles, which, however, must not be confounded with the actual chemical substances of the same name. Quicksilver and sulphur, in the usual sense,

were assumed to be bodies containing maximum amounts of the respective principles. Other Arabian authors held much the same view, but amongst the Christian nations the influence of the Aristotelian doctrine and of a mystical importance attached to the number *three* is noticeable. The third "principle," first assumed by Basil Valentine (fifteenth century), was "salt," the principle of resistance to fire. Some alchemists used different names for the principles; thus Albertus Magnus calls them water, arsenic, and sulphur, and so it is hard to make any serious generalization on the subject. The iatro-chemists naturally paid less attention to the ultimate composition of substances, and this perhaps led to the loosely defined way in which the three principles are referred to by many of the later alchemists; these were, however, always tacitly assumed, and Paracelsus (sixteenth century) asserts that organized as well as inert nature consists essentially of varying combinations of "sulphur, salt, and mercury". Finally Becher (seventeenth century) gave these alchemical elements a new series of names, as appears in the following summary:—

ALCHEMICAL PRINCIPLES.

	Of Metallicity or Durability.	*Of Changeability or Dross.*	*Of Solidification or Resistance to Fire.*
Geber . .	Quicksilver	Sulphur	—
Basil Valentine .	,,	,,	Salt
Paracelsus . .	Arsenic or Quicksilver	,,	,,
Becher . .	Mercurial earth	Combustible earth	Vitreous earth

The lax nomenclature as well as the duplicity of not a few alchemists was scathingly criticized towards the close of the seventeenth century by Kunkel and by Boyle, who was the first chemist to say precisely what he meant by "element," giving at the same time a definition which has lasted: *a substance which has not yet been decomposed into simpler ones* ("Chemista Scepticus," 1661). While suggesting that the then so-called elements were not necessarily simple, he yet predicted a much

larger number of real elements than the Aristotelian four or the alchemistic three, although he doubted if the elements so obtainable by chemists would represent the absolutely ultimate origin of matter.

§ 2. **The Evolution of Chemical Nomenclature**—No further contribution of any permanent value to the problem took place for a century after Boyle's time, for, naturally, so long as people were in error with reference to the supposed phlogiston there was an inversion of opinion as to whether "calx" or "metal" was the real element. As soon as Lavoisier's theory of combustion was definitely accepted the way was open for a sweeping generalization of the host of chemical substances then known. Lavoisier himself undertook the task (1787), adopting as the basis of his system Boyle's definition of an element. With a few modifications he used the nomenclature introduced a little earlier (1782) by Guyton de Morveau, one of the founders of and professor of chemistry in the "École polytechnique" at Paris. This was as follows :—

CHEMICAL SUBSTANCES.

Elements. (Five classes.)	*Compounds.* (Two classes.)
(i) Heat, light, oxygen, nitrogen, hydrogen.	(i) Binary (acids, bases).
(ii) Acid-forming elements (sulphur, carbon, etc.).	(ii) Ternary (salts).
(iii) Metals (we should say "heavy" metals, iron, copper, etc.).	
(iv) Earths (lime, magnesia, alumina, etc.).	
(v) Alkalies (only decomposed by Davy years later).	

Acids and bases, being regarded at that time as combinations of an element with oxygen, were termed binary compounds.

Lavoisier's chief alteration had reference to the last two classes of "elements," of the simple nature of which he was doubtful; indeed, two years later he felt the necessity of eliminating the alkalies entirely from the list of elements. We may

as well complete the story of chemical nomenclature at this point; as we shall shortly see, the discovery of the fundamental rules of chemical combination and the doctrine of "atoms" in its modern form soon followed the adoption of Lavoisier's views. These in turn led to the investigation and accurate analysis of a great many inorganic materials, and in this field no more active and skilful worker existed than the great Swedish chemist Berzelius. His enlightened views and abundant experience fitted him for the work of extending and adapting Lavoisier's nomenclature to include the additional facts known by 1811. In that year he published his first system of nomenclature, based upon his electro-chemical or "dualistic" theory of chemical union (see chap. iv., p. 50):—

CHEMICAL SUBSTANCES.

Elements.		*Compounds.*	
Electro-positive.	*Electro-negative.*	*Electro-positive.*	*Electro-negative.*
Metals.	Metalloids ("non-metals").	Basic oxides.	Acid oxides.
		Salts.	

He tried to extend the dualistic system and its nomenclature to organic compounds, but met with little success in that direction. He also invented a simple method of chemical "shorthand," or abbreviation, which is practically that now in use, and so need not be detailed here. A certain amount of confusion resulted from the fact that Berzelius referred all his formulæ to the "oxygen" standard, or, in other words, took a *bi*valent element as *unit* of combination, and, further, was not definite with reference to the distinction between equivalent and atomic weight. This led him to the use of "barred" symbols to represent what he called "double atoms" in the case of compounds containing two monovalent atoms combined with oxygen; thus he wrote $\bar{H}O$ and not H_2O, and so on. This ambiguity may be the reason why his notation, now universally adopted, was at first received with a good deal of coolness, and, indeed, open

opposition, especially in conservative England. The only other modern notation emanated from Dalton, who assigned to the more common elements various geometrical symbols, and represented their combinations by placing the appropriate symbols in juxtaposition. This method was naturally far too cumbrous to be permanent, though doubtless it was of value in the early struggles of the atomic theory, giving, as it must have done, a mental picture of the way in which the atoms united to form compound bodies.

§ 3. **Discovery of Equivalent Combining Proportions**—Given Boyle's definition of an element and Lavoisier's proof of what substances were elementary and what were compound, it is possible without reference to any further hypothesis to divide chemical substances into the different classes enumerated by Berzelius. This does not apply, of course, to the Berzelian notation, which, as far as its quantitative significance is concerned, is based upon the atomic hypothesis. It only remains now to discuss this important subject and its later development, for all modern work connected with Dalton's theory has so far served to amplify and not to contradict it.

The establishment of the theory is really due to both English and Continental workers. No one has ever questioned that the genius and perception of Dalton led to his enunciation of the doctrine of atoms; it was his idea, and was confirmed by his own experimental work. Nevertheless, when his views were published, it was seen that other and somewhat earlier work afforded strong confirmatory evidence in support thereof.

For instance, J. B. Richter (1791-1800) showed that mixed solutions of two neutral salts invariably remained neutral, whether double decomposition took place or not; he concluded that the two quantities x and y of two different bases X and Y which neutralized the same amount a of an acid A would each neutralize an amount b of another acid B, and conversely. He also measured the different amounts of metals precipitated from salt solutions by certain other metals, and gave to the

whole process the name Stoichiometry—the measurement of the proportion by weight in which substances combine.

Again, in 1808, shortly after Dalton had published his theory, Gay-Lussac published results on the volume relations of reacting gases, showing that the volumes entering into combination bore to each other and to the products (if gaseous) a simple numerical ratio. Thus he proved that

2 volumes of carbon monoxide and **1** volume of oxygen give **2** volumes of carbonic acid.

1 volume of nitrogen and **3** volumes of hydrogen give **2** volumes of ammonia.

He readily perceived in this a confirmation of Dalton's view, while, curiously enough, the latter worker, as we shall shortly see, was inclined to regard it as a stumbling-block.

§ 4. **Dalton's Atomic Theory**—How, then, was Dalton led to the conception of his "atoms"? It came about entirely independently of all this previous work, and, in a more distinctive way than many other famous advances in science connected with different names, was due to the man's own work and thought. He had been analysing olefiant gas (ethylene) and light carburetted hydrogen (methane) and found that, for a given amount of carbon, the latter contained exactly twice as much hydrogen as the former. Struck by the simple relation thus disclosed he proceeded to analyse carbonic oxide and carbonic acid gas, of course with precisely similar results. In this way the *Law of Multiple Combining Proportions* was discovered, and its truth was emphasised still further when he investigated the series of four nitrogen oxides and acids then known.

What did this simple numerical rule imply? Some earlier researches by Dalton helped him towards an answer. In some work on the solubility of gases in water he had, like his contemporary and colleague, Henry, noted how pressure increases the capacity of a gas to dissolve. It seemed as if the water was a mass of minute particles between which the gas particles,

which would be "rarer" and more volatile, could move to a certain extent, and then by increased pressure more of the gas particles would be forced into the interstices of the water-particles. Thus supplied with the rudimentary idea of an atom, it was easy to extend it. If the gases were an assemblage of such particles, in any one gas all the particles must be alike, and moreover any action in which the gas participated must be made up of the actions of the several particles. In other words, when two gases joined to form a third, the process was the result of the union of their constituent particles. It was obvious, too, that one particle of a substance might be joined to one, or to two, or to some other definite number of particles of another substance—thus explaining the rule of multiple proportions. So in 1807-8, the Atomic Theory was enunciated as follows in Dalton's "New System of Chemical Philosophy":—

(1) *Every element consists of homogeneous atoms of constant weight.*

(2) *Chemical compounds are formed by the union of different elementary atoms in the simplest numerical proportions.*

Dalton naturally proceeded to the determination of the relative atomic weights of the elements, assuming that these combined in the simplest possible atomic proportions, and taking hydrogen as the unit of his system. These results, which were not very accurate, expressed therefore the *equivalent combining weight*, and not the atomic weight (in the modern sense of the term).

Dalton's theory differs from the old Greek views of atoms and from Boyle's "corpuscles," which were the ultimate particles of matter and by mutual attraction and repulsion produced chemical combination and decomposition, in that it demands that the atoms of each element are entirely distinct species of matter, and, as first enunciated, places a bar against the notion of an ultimate primary material. He succeeded in showing:—

(*a*) How the elements may be made up of atoms;

(*b*) How these atoms may unite to form compounds;

(*c*) How to determine the relative combining weights of the atoms.

§ 5. **Development of the Atomic Hypothesis**—The conception of atoms was at once accepted by the leading chemists, but most of these (e.g. Davy, Gay-Lussac, Wollaston) perceived that the actual relative weights determined according to Dalton's principles were merely the combining weights, and that no light was thereby thrown on the relative weights of the atoms themselves. There was also the other difficulty arising out of Gay-Lussac's "Law of Volumes"; according to his work on this subject, for instance, one volume of nitrogen and one volume of oxygen gave two volumes of nitric oxide, whilst obviously one atom of nitrogen and one atom of oxygen would give only one "atom" of nitric oxide. The difficulty of an "atom" of nitric oxide occupying twice the volume of the atom of either element was cleared up by the Italian chemist Avogadro in 1811. He assumed that:—

(*a*) Under equal conditions of temperature and pressure, *equal volumes of all gases contained equal numbers of molecules;*

(*b*) There were two sorts of ultimate particles, "molécules intégrantes" (molecules) and "molécules élémentaires" (atoms);

(*c*) The ultimate particles of an element might be molecules composed of more than one atom.

Returning to the previous point, viz. the difference between equivalent weight and atomic weight, we might fill a chapter with a description of the uncertainty and confusion which prevailed in the first half of last century with respect to these two terms. Some, like Davy or Gay-Lussac, held that the determination of the relative weights of atoms themselves was impossible; others, and of these Berzelius was foremost, adopted the opposite conclusion. Berzelius himself attacked the problem with amazing thoroughness, and in the course of ten years had made fairly reliable analyses of compounds of practically all the

known elements. From the equivalents so obtained he chose his atomic weights on the following system :—

(*a*) With elements possessing volatile compounds he made use of Gay-Lussac's and Avogadro's volume-relations.

Thus, starting from 2 volumes of hydrogen and 1 of oxygen giving 2 of water, he saw that in water 2 atoms of hydrogen were united to 1 of oxygen, and so obtained the true atomic weight of oxygen.

(*b*) With other elements he worked on the ratio of metal to oxygen, and assumed that in general only 1 atom of the metal was present per molecule.

In this way he came to regard proportions such as 2 : 3 or 2 : 5 as too complex, and therefore formulated the iron oxides, for instance, as FeO_2 and FeO_3, and not FeO and Fe_2O_3 as at present; so that what we now know to be dyad metals received double, and monad metals received quadruple their present atomic weights.

(*c*) He always took oxygen for the basis of his calculations, and indeed, in his tabulated results, took 100 as the atomic weight of oxygen. (Later on it was thought better to refer all atomic weights to H = 1 as the standard, since hydrogen was the lightest element. In this way the atomic weight of oxygen becomes 15·88, and, since the majority of atomic weight determinations involve the ratio element : oxygen, it has latterly become the custom to call the atomic weight of the latter 16·00, and refer hydrogen (1·008) and all the other elements to this value.)

This first atomic weight table of Berzelius was complete about 1817. We can only briefly summarize its subsequent career.

In 1819 Mitscherlich brought out his "Law of Isomorphism," stating that the amounts of elements which replaced each other in isomorphous compounds were chemically equivalent and represented the relative weights of the replacing atoms, and about 1821 Dulong and Petit showed that in many cases the product of specific heat and atomic weight was a constant number.

Both these rules were of assistance to Berzelius, though he attached but a minor importance to the second.

His second atomic weight table (1826) was rendered necessary because he found reasons for halving many of the values he had previously selected.

Analyses of the chromates showed that chromium trioxide was represented by CrO_3, so that the basic oxide must be Cr_2O_3. Hence ferric oxide was Fe_2O_3 and the "protoxide" FeO, and by isomorphism he deduced similar atomic weights for the allied metals.

Next year, however, doubt was cast on his fundamental assumption that the weights of equal gaseous volumes of the elements were proportional to the atomic weights by the French chemist Dumas, who, by his vapour density measurements (cf. p. 179), obtained in some cases values which were multiples or sub-multiples of the Berzelian numbers. This and the slender basis of Berzelius' assumptions about the atomic composition of compounds led most people to despair of ever finding the relative masses of the actual atoms, and a strong reaction set in against his interpretation of the atomic doctrine.

Between 1830-50 further confusion arose. Gmelin, a German worker, insisted on taking the simplest empirical combining ratios as the equivalents and neglecting atomic weights altogether, thus halving nearly all the Berzelian values. A few years later Gerhardt noted that on this hypothesis more than one equivalent of water or carbonic acid always resulted when one equivalent of an organic compound was burnt, so he decided for the old numbers, except that he regarded all metallic oxides as composed of two atoms of metal and one of oxygen. All three systems were used concurrently by different workers, and a few, not content with the muddle, increased it by calling the equivalent of oxygen 8 but that of carbon 12!

Atomic Weights (O = 16).	*Berzelius* (1818).	*Berzelius* (1826).	*Gmelin.*	*Gerhardt.*	*Final Value.*
Hydrogen . .	1	1	1	1	1
Oxygen . .	16	16	8	16	16
Carbon . .	12	12	6	12	12
Iron . . .	109	54·5	27	27	56
Sodium . .	93	46·5	23	23	23

Fortunately the French chemist Laurent (1843) partially cleared up the confusion by giving precise definitions to the chief terms involved, namely, *equivalents*, the mutually replaceable quantities of similar and similarly combined elements (consequently not always the same for each element); *atoms*, the smallest particles participating in reactions; *molecules*, the smallest particles capable of free existence; *molecular weight*, the weight of a chemical substance occupying the same volume as a molecule of hydrogen. And Cannizzaro in 1858 helped still further by summarizing the methods of atomic weight determination according to reliability as follows :—

(*a*) Vapour-density determination of compounds as well as elements.

(*b*) Specific heat determinations
(*c*) Isomorphism } with due reservation.

§ 6. **The Periodic System**—The inquiry into the manner of union between elements to form compounds has always been closely accompanied by observation of the similarity or dissimilarity of the various elementary bodies. Theories of the mutual relations of the elements have, since the establishment of the atomic theory, developed along two lines :—

(*a*) Discussion of the ultimate composition of the atoms, a problem which we survey a little later (p. 41).

(*b*) Investigation of regularities in the chemical behaviour of the elements.

Until Cannizzaro's systematization of the atomic weight values, only fragmentary evidence of any connexion between properties and atomic weights was available, but instances of apparent relations of this kind were very soon noticed here and there, especially by Döbereiner of Jena, who in 1829 showed that some series of chemically analogous elements could be arranged in "triads" whose atomic weights were in approximately arithmetical progression, e.g. lithium, sodium, potassium; calcium, strontium, barium; chlorine, bromine, iodine. It was also seen that other

triads of very closely related elements possessed almost identical atomic weights.

At about this time the "homologous series" into which so many organic compounds fall were being outlined, and Dumas sought to show that the atoms themselves possibly formed in some way a series based on somewhat similar lines; other arithmetical regularities were pointed out by Odling in 1864. The idea, though ingenious, was not supported to any great extent by facts.

There are no other views sufficiently important to be recorded until after the atomic weight confusion was removed in 1858, but almost within a decade of this advance the *periodic classification of the elements* was accomplished. In its simplest form this, which is the basis of all modern inorganic theory, was stated by Newlands in 1864; he showed that by tabulating the known elements according to increasing atomic weights "each eighth element, starting from a given one, was a sort of repetition of the first" (the "Law of Octaves"), but little serious attention was paid to his discovery in England, and the honour of evolving the complete periodic system was divided five years later between Lothar Meyer of Germany and Mendelejew of Russia.

The former showed that physical properties (atomic volumes) and chemical properties (valency) varied periodically in each group of eight elements and stated that *the properties of the chemical elements are periodic functions of their atomic weights.* The latter drew up a complete table of all the elements known at the time, arranged according to the "periodic law" and attracted much notice by the confidence with which he used his newly found "law" to correct the atomic weights of some elements and to predict in marvellous detail the characteristics of three elements at that time unknown. Both corrections and predictions have been justified, the former in the cases of beryllium, indium, and uranium, the latter by the discovery of scandium, gallium, and germanium.

While the usefulness and general correctness of the system

have been admitted on all hands, difficulties have from time to time appeared and some have not yet been removed. The chief obstacles which have been encountered are :—

(*a*) The groups pass from a strongly electro-positive element (e.g. lithium) through gradually decreasing basic elements and finally reach a strongly electro-negative element (fluorine), after which, without any gradual transition, the next element is again highly electro-positive.

(*b*) The analogous elements of approximately equal atomic weights (such as iron, cobalt, nickel) do not find any suitable place in the table.

(*c*) Some elements of widely varying chemical behaviour are brought into close juxtaposition; such are the alkali metals, silver, copper, and gold.

(*d*) Some closely related elements are separated in the table; such are silver and thallium, or barium and lead.

(*e*) The position of argon and potassium and of tellurium and iodine according to their properties is the opposite of that demanded by their atomic weights.

These objections have been partly met as follows :—

(*a*) The "new" non-valent gases of the atmosphere occupy, from their atomic weights, positions intermediate between the extreme electro-positive and -negative elements, and Ramsay suggested that they form the transition elements previously lacking. It will be noticed incidentally, that the original "Law of Octaves" has become a "Law of Ninths".

(*c*) and (*d*) It is urged that the resemblances or dissimilarities, as the case may be, of the various elements concerned are on the whole best satisfied by their present positions in the table.

(*e*) Many are the re-determinations of the atomic weights of tellurium and iodine which have been carried out in the hope of reversing their order. But the consensus of the results tends to show that the accepted values are correct and that this, together with the argon-potassium anomaly, must be left at present unexplained.

Various difficulties have been at one time or another partly removed by attempts to re-cast the system; among such efforts may be mentioned those of Johnstone Stoney (1888), Walker (1891), and Staigmüller (1902).

In concluding this section, it must be emphasized that Mendelejew's designation of the periodic system as a "law" is somewhat of an exaggeration. The real law which underlies the system has not been discovered, although it may be surmised from the results obtained in the past few years, that the essential principle concerned depends on the constitution of the atoms themselves, upon which question the electronic theory of matter will no doubt in the course of its future development throw considerable light.

§ 7. **Is all Matter derived from one ultimate Fundamental Material ?**—When Dalton's atomic weight numbers were tabulated with reference to that of hydrogen (the lightest) as unity, the values for the few elements then determined were nearly all very approximately whole numbers. There has always been an instinctive desire on the part of philosophers to make simple generalizations wherever possible; it was natural to think that the heavier atoms were made up in some way of a definite number of "condensed" hydrogen atoms. The suggestion is connected with the name of Prout and first appeared in 1815. For a long while it was regarded sympathetically, then gradually the accumulation of evidence against it changed the opinion of chemists, and for years now it has been the custom to speak rather lightly of "Prout's hypothesis". It is pointed out that, firstly, the values on which it was based (Dalton's and T. Thomson's) were hopelessly inaccurate; that, secondly, several workers with a strong prepossession in its favour set out to gather evidence for its support and returned convinced of its untenability; that, thirdly, other workers have tried to invent modified forms of the hypothesis and have usually conspicuously failed. And yet, in spite of the cool reception which Prout's views meet with at the present time,

communications are intermittently appearing in the scientific journals from observers who think they have found a means of calculating the atomic weights of the elements or of indicating how the latter have been "evolved" from a primordial material.

The accurate determination of chemical equivalents by Berzelius and others soon compelled the upholders of the original hypothesis to shift their ground; and in succession the half and the quarter of an atom of hydrogen were put forward as the "unit" of matter. This repeated subdivision of the "unit" of course destroyed the original form of the idea. Dumas, Marignac, and Stas were three noted stoichiometric investigators, each of whom started to collect evidence to bear upon Prout's view, and all concluded that there was no such simple relation subsisting between the elements. Stas, indeed, executed a series of researches which were for all time a model of manipulation and skill: true, of late years sources of error have here and there been detected in them, but every such source of error known to Stas at the period of his work (1840-65) was eliminated with perfect care.

Dumas, whose work was a little prior to that of Stas, and who suggested that the elements formed "homologous series" among themselves similar to the series of hydrocarbons, etc., discovered in organic chemistry, and also Pettenkofer (1850) devised mathematical formulæ whereby to deduce the atomic weights of the heavier from those of the lighter elements, but such equations were scarcely approximately exact.

A few years subsequently there comes a division in the speculations as to the mutual relations of the elements. One line of thought was concerned solely with the resemblances in properties of the various elements and sought to find a working hypothesis by which to be guided in the general problems of chemistry; this helped to lead to the evolution of the "periodic classification of the elements". The other, the more speculative and philosophical line of thought, deals with

the "genesis of matter" and the constitution of the elements themselves.

It may be said that this problem, too, has been approached from two sides: *spectroscopic* and *electrical*.

For a number of years from about 1865 onwards, Sir W. Lockyer made a detailed study of the spectra of the different stars and found that the hottest stars contained chiefly hydrogen and other gases (some then unknown terrestrially), the less hot stars contained the metals with which we are familiar on earth, and the coolest were carbonaceous stars. Again Sir W. Crookes, investigating the "rare earths" obtained from "yttria" (originally supposed to be the oxide of one element, yttrium), split these up into eight different fractions which were in almost every respect chemically alike, but gave different phosphorescent spectra. The former research seems to show that in star-formation a process of building-up of the heavier elements from hydrogen—or something lighter—is going on; the latter that there exist elements so closely related as to be more like "varieties" than distinct "species" of elementary matter. On this basis Crookes in 1886 suggested that the old doctrine of the unity of matter might be true and that all the elements were condensation products of a primary material, "protyle". The fact that Kayser and Runge, and others, have recently shown mathematical or "harmonic" relations to exist between the wave-lengths of similar groups of lines in different elementary "spectra" is held to be further evidence of similarity in the different atomic structures.

On the other hand, Crookes opened up a new line of attack about 1880 by studying the action of electric discharges in vacuum tubes. The "cathode rays," which he was thus the first to study, have since been characterized by Sir J. J. Thomson and others as streams of rapidly-moving matter, as particles whose mass was about the thousandth part of that of a hydrogen atom, and, finally, as particles or atoms of electricity, which has thus itself come to be regarded as material, or rather, we

recognize now that the basis of matter is electrical. Dr. Johnstone Stoney named these atoms "electrons"—a name which has lately become very familiar.

Now, since in electrolysis, etc., a definite amount of electricity is always connected with the liberation of an atom of any element, and also since the "radio-active" metals break down ultimately into these electrons, it has appeared natural to regard the atoms of electricity as the basis of the constitution of the elements, and here we come to the most modern phase of that curious ever-present speculation as to a "primary form of matter".

Most people at present regard the electron as *the* fundamental "stuff" of which "the world is spun," but views differ as to how the different atoms are made from the electrons, and of course there is absolutely no experimental evidence to show. From time to time, suggestions are offered; in 1908 Jessup showed how by addition of groups of electrons to four "protons" or fundamental elements, all the elements in the periodic table could be accounted for, either by building up or by "degradation" of atoms already so formed; in 1909 Egerton put forward the most accurate method of "calculation" of atomic weights yet devised, based on the fundamental assumption of electrons and accurate in most cases to the second decimal place when compared with the best experimental values (his work only applied, however, to the twenty-eight lightest elements, and has been disputed, moreover, by Moir on the ground that the agreements found are due to mathematical necessity).

Chemists have, therefore, made fair progress of late years towards deciding the vexed question of the "unity of matter," but there is still much to be done. The outstanding points of their work in this direction have now been briefly mentioned, and we must leave the story as it is—unfinished.

CHAPTER IV

INORGANIC COMPOUNDS AND THE LAWS OF CHEMICAL COMBINATION

§ 1. **Chemical Affinity and the Manner of Chemical Combination**—The German alchemist, Albertus Magnus, seems to have first suggested the name "affinity" to express the force which leads certain chemical bodies to react with certain others. Ideas as to the nature of the force were in those times prolific and fanciful; Glauber believed the different substances to "love" or "hate" each other, others thought that combination was effected by hooks or pointed prongs on the ultimate particles of matter. Some thought that similar bodies, others that dissimilar bodies, exerted most mutual attraction. The first scientific treatment of the problem occurred when Geoffroy in 1718 tried to construct "affinity-tables," consisting of lists of substances (acids and bases), in order of increasing or decreasing affinity with respect to a fixed base or acid. However, in the phlogistic era little progress was made, because the most important factor—mass—was left out of consideration altogether.

In 1775 Bergmann practically stated that mass made no difference at all, for he said that if, in the case of a substance YZ, the part Y had more affinity for another part X than for Z, then, if X be present, it would become entirely united to Y at the expense of Z, by virtue of its greater affinity. On the other hand, Wenzel in 1777 discovered the "law of mass-action" (which did not reappear till nearly a century later) by

urging that the "amount of chemical action is proportional to the concentration of the acting substance".

About 1801, Count Berthollet declared that the predominant factor in chemical union was the relative masses of the substances concerned and not their affinity; this was of course the diametrical opposite of Bergmann's views, and was based on his conception (and men like Buffon, Newton, and other philosophers, had held the same idea) that the force determining chemical action was identical with gravity. He, therefore, supposed that this, like gravity, was dependent on the masses of the reacting compounds, but pushed his views too far by imagining that *any* (and not definitely "equivalent") masses of two substances could unite to form a third. In the ensuing six years Proust contested his view, and proved by experimental work on the basic carbonates of copper, the two oxides of tin, the two sulphides of iron, and other compounds, that Berthollet was wrong, that combination only took place in constant unvarying proportions, and that if two elements united to form more than one compound, the composition varied by leaps from one proportion to another, and never gradually passed from one to the other. The excellence of Proust's experimental work forced Berthollet to admit he was mistaken, and to modify his theory accordingly. In its modified form, of course, it was correct, for, as has been increasingly recognized, the mass of the reacting substances present plays a very important part in determining the course of a reaction.

Soon after this time the close connexion between electricity and chemical affinity began to be pointed out by Davy, Berzelius, and others, but as this concerns the structure of inorganic bodies rather than the point we are now studying we will leave it for a moment.

During the first half of last century the results of numerous researches tended to support the essential or modified part of Berthollet's theory. For example, H. Rose made an extended examination of the part played by water in various actions

where, given suitable conditions, it can displace relatively strong acids (1842); he showed how in some cases (iron, mercury, etc.) basic salts are formed in presence of excess of water, while in others (alkaline sulphides) complete hydrolysis may occur. Somewhat later he discussed the influence of the varying proportions of the reacting compounds in cases of "double decomposition," and in 1855 Gladstone published important results dealing with the same class of reactions.

Meanwhile, in 1850, Wilhelmy devised a formula to express the rate of "inversion" or hydrolysis of cane sugar which is essentially an enunciation of the modern form of the "law of mass action". Further data towards this end were provided by the elaborate work of Berthelot and Péan de St. Gilles from 1861 to 1863 on esterification; they showed that, starting with equimolecular amounts of alcohol and acid, or of the corresponding ester and water, the same mixture of alcohol, acid, ester, and water will finally be reached, and that the final composition of this mixture can be altered according to simple rules by increasing the acting mass of any of the constituents. On the other hand, thermo-chemical evidence which, again, helped to support the law of mass-action, was given by Julius Thomsen at varying times from 1854 to 1868. The most complete statement of the matter is always associated with the names of two Norwegian investigators, Guldberg and Waage. Supported by the facts which have just been summarized, and basing their arguments on Berthollet's proposition that "chemical equilibrium depends not only upon the affinity, but also essentially upon the relative masses of the reacting substances" (Nernst, "Theoretical Chemistry"), they affirmed that in all chemical actions the amount of action is proportional to the acting mass. Since we are merely treating the subject historically, it is impossible to give the details of their argument, but we may reproduce the familiar equation which represents the velocity V with which a given reaction will proceed:—

If substances of concentration $c_1c_2c_3 \ldots$ *are reacting to form new substances of concentration* $c^1{}_1c^1{}_2c^1{}_3 \ldots$, *then*

$$V = kc_1c_2c_3 \ldots - k^1c^1{}_1c^1{}_2c^1{}_3 \ldots$$

where k, k^1 *are numerical constants; thus when equilibrium is attained,*

$$c_1c_2c_3 \ldots = Kc^1{}_1c^1{}_2c^1{}_3 \ldots$$

The treatise "Études sur les affinités chimiques" (1867) in which these results appeared remained comparatively unnoticed for some time, and indeed the generalization was subsequently made by other chemists, but in its most extended form it was developed, as we have said, by Guldberg and Waage. Van't Hoff (1877) and Horstmann (1869-77) succeeded in making approximately the same generalization in perhaps a more strictly logical or deductive manner from thermo-dynamical and mathematical considerations.

There have been a number of studies published on the subjects of affinity and mass-action since the law was definitely stated in 1867; these are dealt with in Chapter x.

It will be seen that the terms chemical statics and dynamics are by no means fanciful, for nowadays the problem of chemical affinity has been reduced, so to speak, to mathematical equations and numerical constants, and by such rigid means as these a knowledge of *how* the forces producing chemical charge act is being rapidly gained, but when it is asked *what* are these forces and *why* do they so act, we cannot tell.

Having now outlined the work done on the general question of the rules of chemical reaction and formation or decomposition of compounds, we turn to the other aspect of the problem, viz. how are the various atoms joined, each to the other, in chemical compounds? It will be convenient to restrict ourselves for the time being to inorganic compounds, for the theories of the structure of organic substances are in a far more advanced state than those of the former.

§ 2. **The Structure of Inorganic Compounds**—The purpose of this book prevents us again from dealing with the oldest views of structure, and we must confine ourselves to the

more modern facts and theories, which are certainly no less interesting.[1]

As chemists, however, we have to pay attention to present facts rather than past fancies or future chances. The facts upon which the structure of compounds depends are primarily the "laws" of constant and multiple combining proportions. We will call to mind then, how the former was definitely proved by Proust in 1801-7 (p. 46), and the latter also foreshadowed in Proust's work and definitely established by Dalton about 1808 (p. 33). With the united help of these laws and of Dalton's atomic theory, it seemed so easy to most chemists in the early decades of last century to devise formulæ for all manner of compounds. And so it was, indeed, very easy; but whether the formula bore any relation to the chemical behaviour of the compound in question was often quite another matter, and in not a few cases the older formulæ absolutely fail to express the facts at all. In short, the problem of the structure of inorganic compounds was for a long while thought to be much more simple than it really is.

The view that there was a mutual connexion between heat, electricity, and chemical force came to the front about 1800. Twenty years previously, Galvani had noticed the action of an electric current on the frog, and Volta had extended the knowledge of electricity considerably, had devised his "Pile," and had suggested that friction of two dissimilar bodies was sufficient to endow them with electricity of opposite polarity. In 1807, Davy elaborated this view by holding that the smallest particles of substances (atoms) become oppositely electrified upon con-

[1] There is a curious attraction about the old fanciful notions of many of the alchemists and phlogistic chemists which seems to make the story of their work much more interesting to read than that of later and present-day chemists; perhaps the underlying cause is the same as that which makes a novel appeal to most people more than a history book, or, judging from current magazines, which renders the possibilities of "radium" or "electrons" more attractive to the "lay mind" than, shall we say, the constitution of quinine or the law of mass-action.

tact (the intensity of electrification rising with increase of temperature), and that chemical combination results from neutralization of the opposing potentials. The sign of the potential of the combining elements could be experimentally determined, electro-positive elements being isolated upon electrolysis at the negative pole, and vice versa.

In 1812, and more fully in 1819, Berzelius published the dualistic theory of chemical combination, which resembled Davy's in some fundamental points, but differed in that it was more systematically developed. He assumed that every atom possesses both $+^{ve}$ and $-^{ve}$ electricity, but in varying amounts. Thus some elements were positive, others negative, most were positive with respect to some, and negative with reference to other elements; oxygen only was never positive to any element, and so was held to be purely electro-negative, and for this and other reasons was adopted by Berzelius as his standard or starting-point. The elements by combination furnished new bodies in which again an excess of one or other kind of electricity was present. Thus basic oxides came from the union of oxygen and strongly electro-positive elements (metals), and acid oxides from oxygen and the metalloids. This tended to confirm Lavoisier's view (p. 26), that all acids contain oxygen. Salts, and furthermore mixed salts and hydrated salts, were regarded as the product of union of the already compound bases and acids, an excess of one or other kind of electricity being always left over, but in less pronounced quantity than with simpler substances. This important theory served well to point out the constitution of the most obvious classes of inorganic compounds, viz. bases, acids, and salts. Berzelius, however, tried to push it further and attempted to systematize the organic compounds then known on the same basis. Until about 1840 his efforts met with complete approval, and the dualistic theory held practically universal sway. Soon afterwards it began to decline, chiefly through the influence of the following facts:—

(1) In 1834 Dumas discovered the phenomena of "substitu-

tion" in organic chemistry, by which a strongly negative element (chlorine) *replaced* electro-positive hydrogen.

(2) In 1839 Daniell showed that in the course of electrolysis the same amount of electricity will set free a definite amount of hydrogen on being led successively through water and a solution of sodium sulphate, but also, in the latter case, will liberate an equivalent of sodium hydrate, thus doing double as much work in the second as in the first instance, according to Berzelius' theory.

(3) The dualistic hypothesis did not precisely explain why certain acids not containing oxygen (notably HCl) were as strong or stronger than many oxygen acids, containing the most electro-negative element of all.

Many objections to the dualistic theory therefore arose about 1845-50, and, as usual, the reaction carried opinion to the other extreme, and it was sought to regard inorganic compounds as simply composed of the different "units" of atoms, in a similar manner to the way in which the structure of organic substances was beginning to be regarded at that time. The French chemists, especially Dumas and Wurtz, took the most prominent part in developing the "unitary," as opposed to the dualistic, idea.

§ 3. **Valency**—This word is synonymous with the terms "replaceable value," "atomicity," "saturation-capacity," and, like some other terms occurring at different periods of chemical history, it has tended to become somewhat of a nuisance and to enforce conceptions entirely beyond its real simple meaning. It is a name for the "combining worth" of an element, expresses the number of equivalents of a "univalent" element with which the element in question can unite, and, as E. Meyer has said, is really nothing more than an expression of the laws of definite and multiple combining proportions.

In 1834 Dumas showed in connexion with his substitution researches that one "atom" of chlorine replaced one atom of hydrogen, but that the latter was replaced by only a "half atom"

of oxygen. A little later Liebig noted that an antimony atom can combine with three atoms of hydrogen, whereas the potassium atom is equivalent to only one, and he also developed the knowledge of polybasic acids, showing that some acids contain only one and others (e.g. citric acid) more than one replaceable hydrogen atom. This brings out the idea of the *equivalent* as distinct from atom or molecule, and in 1843 Laurent gave definite expression to the term, and stated that elements could possess varying equivalents under varying conditions.

The idea of a constant combining worth for each element was, however, very popular in those days, and Wurtz, for example, formulated numbers of inorganic compounds on the hypothesis that the elemental valencies were always fixed. Such formulæ, which quite failed to represent the chemical behaviour, and were simply strings of letters, such as HOOOCl for chloric and HOOOOCl for perchloric acid (to give only one instance), prevailed in "text-books" for many years, and have not absolutely died out even at the present day. Kolbe wrote in favour of a "maximum valency" of each element in 1854—indicating the existence of possible cases where all the "valencies" were not utilized. At about the same time papers were being published on the subject in England by Williamson and by Odling. Williamson's work was more concerned with the constitution of organic compounds (cf. chap. vi.), while Odling discussed the different combining powers of iron and tin, as shown in their varying oxides, and introduced, by the way, the term "replaceable value". His adhesion to the "type" theory of organic compounds, by means of which he tried to classify inorganic acids, presumably prevented him from arriving at such conclusions as those deduced by another English chemist, Frankland. It is to the latter, indeed, that the clearest ideas about valency at this period are due. This work dates from about 1853 onwards, and his views were generally accepted by the year 1860. He noted how nitrogen, phosphorus, antimony, and arsenic behaved sometimes as tervalent and sometimes quinquevalent, and was,

therefore, led to regard them as analogous; for similar reasons he classed carbon, silicon, titanium, and zirconium together, etc. He did more than any of the contemporary workers to give a definite meaning to "valency" or "saturation-capacity," as he called it: he showed how circumstances influenced the combining capacity of the elements, so that an element which under given conditions evinced no tendency to behave otherwise than, say, tervalent might, in other cases possess another valency. He argued that such substances would possess a maximum "saturation-capacity," but that all its possible "valencies" would not invariably come into action. This method of classifying elements according to similar combining power was, of course, a step in the direction of the "periodic classification," which we have already discussed (p. 38).

On the Continent, on the other hand, events moved somewhat differently. Gerhardt put forward views similar to Frankland's as early as 1856, but in 1860 Kekulé, arguing from the "organic "point of view, declared for the principle of constant valency. Blomstrand, Kolbe, and others debated the point during the next five years, the result being the confirmation of Frankland's theory. Erlenmeyer, about 1863, made an important statement, which was in the main the same as Frankland's, but extended the latter by the conception that valency was due to the number of "points of affinity" possessed by each element. This has had a somewhat unfortunate sequel, for it is probably the innocent cause of the excessive emphasis which has so often been laid on the modern "structure-formulæ," in which union is depicted by dashes. It is interesting to speculate how many people have consciously or unconsciously conceived the dashes as an image of the real mode of union of atoms. The signs mean nothing except that one atom is "united" with the next—*how* precisely no one knows.

The point as to whether all the affinities of a polyvalent element are of equal worth has been pretty thoroughly discussed since the modern idea of valency took firm hold. The experi-

mental investigation has centred round derivatives of carbon (Roscoe and Schorlemmer, Henry (1888)), sulphur (Kruger, Klinger), and nitrogen (hydroxylamine derivatives, etc., by Lossen, Beckmann).

This simple conception of valency, however, is not enough to explain many facts which have come to light of late years. These new points generally concern the structure of organic bodies, but for the sake of compactness will be presented here. The reactions of substances written as $R.CH=CH.CH=CH.R^1$ are quite anomalous according to this formula; on reduction or addition of halogen they yield $R.CHX.CH=CH.CHX.R^1$ exclusively, and *not* $R.CHX.CHX.CH=CH.R^1$. In 1899 Thiele suggested that the affinities of elements were not always completely utilized, that in "unsaturated" compounds, compounds possessing "residual affinity," the carbon must be represented as possessing "partial valencies," and that a better method of graphically representing them was

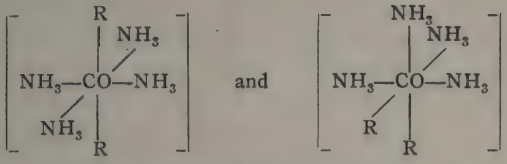
$$R.CH=CH—CH=CH.R^1.$$
$$\vdots \quad \vdots \quad \vdots \quad \vdots$$

Assuming that the central "partial valencies" saturated each other he arrived at the formula

$$R.CH=CH—CH=CH.R^1 \rightarrow R.CHX.CH=CH.CHX.R^1.$$
$$\vdots \qquad\qquad \vdots$$

Again, complex salts of various metals are known which cannot be readily accounted for by the simple valence theory. Werner has advanced the view that such compounds (cobaltammines, cobalticyanides, etc. etc.) must be represented by a new method. Taking a concrete example, the following cobaltammine chlorides are known, the chlorine atoms outside the bracket being the only ones which become ionized in solution: $[Co(NH_3)_6]Cl_3$, $[Co(NH_3)_5Cl]Cl_2$, $[CoCl_2(NH_3)_4]Cl$, and, finally, non-ionized bodies, such as $[Co(NH_3)_3(NO_2)_3]$. So far, as Blomstrand and Jörgensen showed long ago, there is no need to go beyond ordinary structure formulæ, but some com-

pounds of the type $[Co(NH_3)_4R_2]X$ each exist in two different forms, of characteristic colour. Werner attributes this to a new kind of stereoisomerism of the group within the square brackets thus :—



This mode of union he calls "co-ordination," to distinguish it from the usual union, expressed in terms of ordinary "valency". Jörgensen, however, disputes the method of representation entirely, and since doubt also exists as to the correctness of some of the alleged observed facts, the matter must be left at this point.[1]

The whole subject of valency is thus still very unsettled; it seems of late years as though the solution of the problem will ultimately be upon an electrical or electronic basis.

In 1904 Abegg put forward the view that each element is potentially octovalent, the eight valencies being made up of positive and negative ("normal" and "contra") valencies, as follows :—

Periodic Table Group.	I.	II.	III.	IV.	V.	VI.	VII.
Normal . .	+ 1	+ 2	+ 3	+ 4	− 3	− 2	− 1
Contra . .	− 7	− 6	− 5	− 4	+ 5	+ 6	+ 7

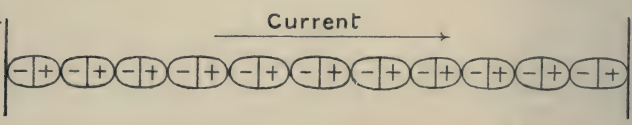
The extent to which the contra-valencies come into play depends partly on the nature of the atom itself, partly on the circumstances of its combination. This hypothesis is more or less a precursor of the purely electronic view.

[1] Other views, involving less profound modification of existing ideas on valency, have been recently put forward by Friend (1908), Sir William Ramsay (1908), and Miss Baker (1909), in order to explain the structure of the metallammino derivatives,

In 1907 Sir J. J. Thomson suggested that elemental valency depends on the transference of electrons to or from the element atoms by the action of other element atoms, so that the "valency lines" really portray tubes of electric force towards or away from the atom. This view is being extended to the structure of organic compounds, and it is evident that it marks an advance upon the older theories, since it is a step in the direction of a hypothesis which may eventually present an explanation of all the varied problems of chemical structure and unite them into one simple theory. At present it appears difficult to get enough experimental evidence upon which to base an universal electronic theory of chemical composition.

§ 4. **Electro-chemical Theories**—It will be best to give at this point a collected account of the various hypotheses developed during the last hundred years with reference to electro-chemical decomposition. The general electrical theories of Davy (1807) and Berzelius (1812-40) have already received attention (pp. 49, 50), but the more particular explanation of the phenomena of electrolysis remains to be dealt with.

The theory which found its way into text-books for many years was that of Grotthus (1805), according to which the electrolyte molecules, previously indiscriminately distributed through the solution, arranged themselves in "chains" through the liquid under the influence of the electric current, the particles adjacent to the electrodes then separating, thus :—



In 1854 Clausius applied the kinetic theory (which he had recently developed in the case of gases) to electrolysis. He assumed that the electrolyte molecules were in constant motion in the solution (a view previously expressed in more general

terms by Williamson in his work on the ethers ; cf. p. 84), and that consequently they were momentarily split up into their ions (to use the convenient modern term). Under ordinary circumstances recombination took place at once, but in presence of a current the ions were separated at the electrodes, a mutual interchange of component parts ensuing between the dissolved molecules between the electrodes. The objection to both theories is that each presupposes a certain minimum electric force to be necessary for electrolysis, whereas the smallest current will effect electrolytic decomposition.

The next great advance was the "ionic theory" of electrolysis, established by Arrhenius in 1887, and foreshadowed as early as 1833 by Faraday. The latter scientist outlined the two chief "laws" of electrolysis (the amount of chemical action is proportional to the amount of electricity, and chemically equivalent quantities of all ions are set free by the same quantity of current), introduced the terms "ion," "anion," "cation," and was convinced that "the power which governs electro-chemical decomposition and ordinary chemical attractions is the same," and that the force acting upon the ions was "either superadded to or *giving direction to* the ordinary chemical affinity".

Arrhenius supposed that all electrolytes (according as they are "good" or "bad" conductors) are more or less dissociated in solution into ions carrying charges of "positive" or "negative" electricity in proportion to their "valency". The electric current simply acts as a directing force, causing the ions to migrate to either electrode and then to deposit their electric charges, after which they reappear as the usual chemical elements or groups, and may be then set free as such, or undergo further chemical decomposition with the electrode or the solution. This view found great support from other physico-chemical evidence, notably when Ostwald showed, by widely extended instances, that the electrical conductivity or affinity coefficient of acids and bases gave exactly the same order of

strength as that determined by a variety of physical and chemical methods (cf. p. 177).

Another modern theory of electrolysis, the "hydrate" theory, must also be mentioned, but this is not apparently destined to have a great influence on chemical theory.

The latest advances deal with the extension of the ionic theory, owing to the conception of the materialistic nature of electricity. When "negative" electricity was first shown to be material, it was naturally anticipated that there would be a corresponding "positive" electricity as well, but later work points to the conclusion that there is only one kind of electricity—"negative electricity," or, using modern terminology, electrons. Consequently a certain amount of readjustment of the theories of electrolysis has become necessary, and this has lately been effected, notably by Ramsay (Presidential Addresses to the Chemical Society, 1908-9). It is suggested that the elementary atoms are combined with electrons in two ways—with "active" and with "latent" electrons. The number of latent electrons depends on the maximum valency of the element and the particular valency displayed in a given instance, while the active electrons are the cause of the displayed valency.

Suggestions of a somewhat similar kind have also been made recently by Kauffmann, Stark and other chemists. Stark's view of the process involves the assumption that neutral water molecules are added to the ions, and thus accounts for the phenomena of hydration of the ions.

CHAPTER V

NOTES ON THE HISTORY OF THE ELEMENTS AND THEIR CHIEF COMPOUNDS

HAVING discussed the general development of our views relating to the nature of elements and the manner of their chemical combination, we must devote a few pages to a description of the chief inorganic substances. In some cases there are interesting points connected with the discovery of an element or the production of a new compound, but as a rule the discovery of a particular substance is of very minor importance when compared with the principles governing the work in question or with the systematization of a class of compounds or of chemical reactions. We shall accordingly pay greater attention to the latter two lines of research, giving at the same time incidental prominence to the history of individual substances. The confusion, prior to about 1790, between elements and compounds has been previously mentioned, so that it will be readily understood that although numerous inorganic or mineral substances were known long before that date, their systematic history only commences with Lavoisier, who classified mineral bodies into acidic and basic oxides, salts and elements. We will review them in this order, adding further sections upon the development of mineralogy, and the comparatively recent advances in radio-activity and the knowledge of the metals of the "rare earths".

§ 1. **Acidic Oxides**—When Lavoisier overthrew the phlogiston theory he established in its place a system in which

oxygen played much the same part as the hypothetical "phlogiston" in the preceding era—oxygen was the central point of his chemical system, since it united with every element known to him. Referring to his system of nomenclature (p. 30), we see that he called the compounds of the metals with oxygen, oxides or bases, while those of oxygen and the metalloids ("non-metals") were termed acids. He held oxygen to be an essential constituent of all acids, and gave it its name (acid producer) accordingly. Berzelius modified these views by assuming that oxygen was the most electro-negative element, all others being electro-positive with respect to it. The acidic or basic properties of the oxides, therefore, depended upon the excess of negative electricity possessed by the oxygen or of positive electricity possessed by the combining element; this view again required the presence of oxygen in all acids. The halogen acids, such as hydrochloric (muriatic) were supposed to be compounds of hydrogen and a halogen; the latter substances were assumed to be oxides of hypothetical elements. However, since the halogens had never been split up into simpler substances, they were, according to Lavoisier's definition of an element, elements, and efforts were soon made in the case of chlorine to decide whether it was really a compound. About 1810 Gay-Lussac and Thénard, in France, and Davy in England, made attempts to decompose that gas in various ways, but without any success, and Davy decided that it was an element, and gave it its present name in distinction to Berthollet's misleading title of "oxymuriatic acid". He pointed out that in the following three reactions it behaved exactly like an elementary substance :—

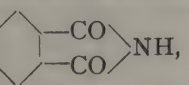
1 vol. Hydrogen + 1 vol. Chlorine → 2 vols. Hydrochloric Acid.
1 vol. Hydrochloric Acid + Sodium → Common Salt + ½ vol. Hydrogen.
Sodium + Chlorine → Common Salt.

Gay-Lussac and Thénard also adopted this opinion, but Berzelius held out against it for a long while. It naturally

spoiled the oxygen-acid theory; it helped to overthrow the dualistic hypothesis.

Davy himself, as a matter of fact, stated that hydrogen and not oxygen was the essential constituent of acids, since anhydrides (e.g. iodic anhydride) were not acid except in presence of water.

The next notable point in the history of acids came several decades later, and consisted of Graham and Liebig's work (already referred to, p. 52). Graham showed that phosphoric and arsenic acids each exist in three forms, according to whether one, two, or three molecules of water were combined with one molecule of the acid anhydride. Liebig proved a similar fact a little later, when he showed that many organic acids (citric, cyanuric etc.), were polybasic. In this case the dualistic explanation, based on the addition of fresh molecules of water, was cumbrous, and Liebig soon saw that a clearer view was obtained by the hydrogen-acid theory, the polybasicity being explained by the presence of more than one replaceable hydrogen atom. This was really the first contribution to the modern theory of valency.

After the general adoption of the hydrogen-acid theory (about 1855) there is little to be recorded in the development of views in this direction, except that Arrhenius' ionic theory extends the conception still further by suggesting that the characteristic properties of acids are due, not to elementary but to ionic hydrogen, H^+. At the present day the most general definition of an acid is a substance containing hydrogen replaceable by metals, an expression which includes many organic bodies (e.g. phthalimide  , malonic ester $CH_2(COOC_2H_5)_2$, etc.), and also such metallic hydroxides as $Al(OH)_3$, $Zn(OH)_2$, etc., which form sodium salts in presence of alkali.

The following acids deserve special attention :—

Sulphurous.—Properties of burning sulphur known to Homer and Pliny; SO_2 isolated by Priestley.

Sulphuric.—Known to Geber; preparation from iron vitriol described by Basil Valentine.

Nitric.—Known to Geber; method of preparation by Basil Valentine; constitution due to Cavendish.

Carbonic.—Known as a distinct gas to Paracelsus and v. Helmont; constitution due to Black and Priestley.

Muriatic.—Known to Basil Valentine (*spiritus salis*); preparation from salt and vitriol by Glauber.

Aqua regia.—Known as a mixture of *aqua fortis* and *spiritus salis* to Basil Valentine.

Phosphoric.—Discovered by Boyle (1693); investigated by Marggraf, Scheele, Gahn.

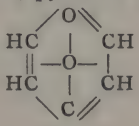
Boric.—First prepared and its salts characterised by Homberg (1702).

Hydrofluoric.—Used for etching glass by Schunhardt (seventeenth century), but without knowing its constitution; worked out by Gay-Lussac and Thénard, Berzelius, Ampère; first prepared pure in 1869 by Frémy.

The *acids and anhydrides of chlorine* ($HClO$, $HClO_3$, $HClO_4$) were investigated by Davy, Balard, Roscoe and others during the first half of last century, but it is comparatively recently that their constitution and that of other halogen oxy-acids has been systematically explained by the progressive increase in valency (from one to seven) of the halogen.

The majority of the more complicated inorganic acids (*ferrocyanic, sulphocyanic, polythionic*, etc.) have only been studied within the past century. Gay-Lussac and Davy were among the first workers in this field; Balard, Liebig, Wöhler, and Roscoe are other prominent names which must be mentioned. Attention should be paid to the numerous researches on "per" acids (cf. p. 72) carried out during the last few decades.

§ 2. **Basic Oxides and Metallic Salts**—The knowledge of metallic oxides has for the most part grown parallel with that of the acids; the characteristic properties of alkalies (the stronger bases) were known to the earliest alchemists, while Lavoisier defined bases as the oxides of the metals, and Berzelius assumed them to be substances in which the electro-positive strength of the metal overcame the electro-negative force exerted by the oxygen. The possibility of polyacid bases followed as soon as the doctrine of polybasic acids was established

by Graham and Liebig, while finally, with the advent of the ionic theory, the characteristic reactions of bases were seen to depend on the presence in solutions thereof of the hydroxyl ion OH^-. The term "base" extends of course to-day to all substances capable of possessing such an ionizable hydroxyl group, for instance, ammonium hydroxide $N\overline{H}_4OH$, pyridinium $C_5H_5NH.OH$, sulphonium hydroxides $R_3S(OH)$,  phosphines R_3P, pyrones and so on.

Curiously enough, the modern view of a salt was practically arrived at during the phlogistic period through the work of Rouelle and Richter. Rouelle (1744) defined salts (neutral, acidic, and basic) as the substances formed by the union of an acid and an alkali, and Richter (1791) discovered the laws governing the neutralization of acids and bases (cf. p. 32). It was therefore simply necessary for Lavoisier to adjust the terms to his new oxygen theory, and to point out that in his system salts were ternary and not binary compounds like the acidic and basic oxides. Berzelius also explained salt-formation as the result of the union of electro-positive and -negative oxides, pointing out the apparent confirmation of his theory in the electrolytic resolution of salts (such as sodium sulphate) into acid and alkali. He tried to account for double salt formation and the existence of water of crystallization by the assumption that even in salts there remained a slight excess of one or other kind of electric polarity. The final modern view of salt formation may be illustrated by the typical ionic equation :—

$$\underset{\text{base}}{R^+ + OH^-} + \underset{\text{acid}}{H^+ + X^-} = \underset{\text{salt}}{R^+ + X^-} + H_2O.$$

Before glancing at a few bases and salts of historic interest, we may discuss the relations of the alkaline carbonates to the

alkalies. This was a source of great misunderstanding to the alchemists and phlogistonists, many of whom seemed to look upon the alkaline carbonates as elementary bodies which passed into the alkalies (alkaline calces), e.g. :—

Chalk + phlogiston → lime.
Lime (i.e. chalk + phlogiston) + potassium carbonate → caustic potash + chalk.

The researches of Joseph Black (1755) cleared up the whole matter, for he showed that :—

(*a*) Limestone or chalk lost weight by calcination and yielded a gas ("fixed air") identical with van Helmont's "gas sylvestre".
(*b*) The "mild alkalies" (alkaline carbonates) could also be made to yield this gas by the application of acids.
(*c*) The "mild alkalies" on treatment with lime became "caustic," and at the same time chalk was formed in the proportion of chalk : lime, as had been found in the reverse direction in experiment (*a*).

These results led him to the modern interpretation of the relations subsisting between lime and chalk, magnesia, and magnesium carbonate, and the "caustic" and "mild" alkalies.

The following description of the discovery of the more notable metallic oxides and salts may, although not exhaustive, be of interest :—

The *Ancients* were acquainted with soda and potash, lime and magnesia, and the corresponding carbonates ; with rock salt, saltpetre, copper, vitriol, alum, cassiterite (SnO_2) and others of the more plentifully occurring minerals. Naturally, however, there was little or no distinction drawn between closely allied bodies such as soda and potash or limestone and magnesite ; magnesia, alum, and lime were not definitely distinguished by the alchemists or iatro-chemists, and it was not until Scheele's time that baryta ceased to be regarded as a casual variety of lime.

As might be expected from the development of experimental research during the *alchemical era*, a great many artificial preparations, as well as numerous naturally occurring compounds, were discovered by the metal-transmuters and their successors, the iatro-chemists. To the *first alchemical period* belong the discoveries of ammonium chloride (salmiac, Geber), carbonates (from urine ; and, by Basil Valentine, from salmiac and potashes),

copper oxides, acetate (verdigris), and sulphate (preparations by van Helmont and Glauber), silver nitrate (lunar caustic), gold chloride (from aqua regia and gold); of calcium sulphate (gypsum, etc.), mercuric oxide (Geber), mercurous chloride (calomel, Geber, improved later by Croll), corrosive sublimate (Geber); of the various alums (Basil Valentine; all these were much confused with each other and with iron vitriol, $FeSO_4$), lead oxides (litharge and minium), sulphide, and carbonate (white lead, with which various salts of zinc were confounded). The oxides and acids of arsenic were known to Geber and Albertus Magnus, and Basil Valentine investigated numerous compounds of antimony and of iron.

The *iatro-chemists* were responsible for the investigation of sodium sulphate (*sal mirabilis*, Glauber, 1658); zinc oxide (Libavius), chloride (as an oil, Glauber), sulphide (Agricola) and sulphate (vitriol), distinguishing these from the similar lead compounds; mercuric sulphate (turpeth, Paracelsus); stannic chloride (spiritus fumans Libavii, Libavius), lead and ferric chlorides (Glauber), and the lead acetates (Libavius).

During the *phlogistic* period a considerable amount of the confusion between similar compounds such as potassium and sodium sulphates or lime, magnesia, baryta and alum was removed, and a clearer knowledge of the following amongst many other substances resulted; the sulphates of potassium, magnesium (Crew, 1695), aluminium and iron; calcium chloride and nitrate; strontium carbonate (strontianite, Crawford, 1790); the various oxides of manganese (Scheele, and much later, in the nineteenth century, Liebig and Wöhler, Mitscherlich and Franke) and of iron (Proust, and comparatively recently, Frémy on ferrates).

We thus arrive at the modern epoch of inorganic chemistry, in which a most prominent part was played by Berzelius and his students. These very thoroughly investigated, from about 1820 onwards, the compounds of titanium, zirconium, thorium, chromium, molybdenum, tungsten, uranium, and other then recently discovered metals; Roscoe also added to the knowledge of the halides of tungsten, while its complex oxy-acids received attention from Margueritte, Marignac and others. We may also mention, amongst a mass of other work, the researches on copper sub-oxides (Rose and Thénard), on silver sub- and per-oxides (Wöhler), and on the complex ammonia-metallic salts of cobalt (Rose, Frémy, Jörgensen, and latterly Werner), chromium (Christensen, Pfeiffer), rhodium (Jörgensen), iridium (Leidié) and platinum (Magnus, Jörgensen).

§ 3. **Mineralogy**—Our historical survey of inorganic compounds would be incomplete without reference to the study of naturally occurring bodies as distinct from those manufactured in the laboratory. Of course in olden times the overwhelming

bulk of substances known were minerals (limestone, marble, rock salt, etc.), since experiment played such a minor part in the chemistry of the ancients. Various ores and precious stones became known as time went on, and when, at the close of the phlogiston era, the importance of gravimetric analysis was realized, several chemists of note found scope for their energies in laborious but necessary analyses of the minerals then known. Bergman, Scheele, Klaproth, Fourcroy, and Vauquelin gave especial assistance in this field, their researches showing that minerals obeyed the same laws of constant and multiple proportions as synthetic compounds. At this time, too, efforts were made to classify minerals, but chiefly according to their physical properties, their chemical relations being almost neglected. The most noteworthy of these earlier mineral systems were those due to Werner and to Häuy of Paris, towards the end of the eighteenth century. The latter based his classification chiefly on similarity in crystal form (cf. "Crystallography," chap. x.).

Bergman, on the other hand, emphasized the importance of the chemical composition of minerals, although in his day so little was known of this side of the question.

The most thorough classification of minerals, however, was due to Berzelius, who in 1812 showed that their composition was in entire agreement with Dalton's atomic theory, and that they were inorganic compounds of exactly the same order as any prepared in the laboratory. In 1824 he produced a mineral system, based on the dualistic hypothesis, dividing minerals into non-oxidized and oxidized compounds. Although various modified classifications have since appeared from time to time, these present no fundamental difference from that of Berzelius.

The nomenclature of minerals has never been properly systematized, for they are still named according to individual peculiarity, or to the locality where first found, or in order to perpetuate the names of their discoverer or his friends, but rarely so as to show somewhat of their chemical composition.

During the past 100 years mineralogy has been characterized

by attempts to synthesize minerals (a kind of chemical geology) and by the systematic investigation of newly discovered ones.

Amongst the synthetic efforts must be mentioned the conversion of chalk to marble (Hall, 1801), the artificial preparation of arragonite (G. Rose), Bunsen's researches on the geysers of Iceland, Van't Hoff's studies with reference to ocean deposits, and, finally, the comprehensive work of a school of French chemists, represented by Sénarmont, Lévy, Friedel, Berthelot, and Moissan. These have reproduced in the laboratory the formation of quartz, etc., by slow double decomposition in solution; the slow crystallization of dilute solutions (gypsum, etc.); the action of water under high pressure at varying temperatures; and the formation of minerals in the interior of the earth or in prehistoric times by the action of intense heat, with or without an accompanying enormous pressure (Berthelot, Moissan); the preparation of carbides, nitrides, etc., in the electric furnace, the interchange of allotropic forms of the elements (e.g. production of small diamonds, etc. etc.).

New minerals have been found both as the result of geographical exploration and of more thorough examination of previously known deposits. Examples in the first category may be taken from the discovery of platinum and allied ores in South America, of new ores (along with tin and other known metals) in Borneo, of gold in various continents (Africa, Australasia, North America), and (recently) of numerous rich deposits of silver, cobalt, and many other metals in Northern Canada.

Berzelius and his co-workers discovered many ores containing chromium, molybdenum, vanadium, and allied metals; Mosander in 1841, and many workers since, have investigated the ores of yttria, gadolinite, etc., occurring chiefly in Scandinavia and Greenland. About fifty years ago the deposits of soluble salts at Stassfurt (near Magdeburg) were discovered, and have been extensively utilized in many ways (manures, preparation of magnesium, potassium, etc.); they consist mainly of chlorides

and sulphates of potassium, magnesium, sodium, and calcium. Of late years a notable class of minerals has been studied, viz. those containing occluded gases, usually hydrogen, nitrogen, carbon dioxide, helium, and sometimes argon and neon (clevéite, malacone, gadolinite, etc.). The chemical examination of meteorites must not be forgotten, since this has confirmed the spectroscopic evidence that extra-terrestrial bodies are for the most part made up of the same elements as our own planet (Wöhler, Wolcott Gibbs).

§ 4. **The Chemical Elements**—The preceding paragraphs will have shown clearly that in the majority of cases the discovery of an element was long preceded by a knowledge of its compounds, and that, further, the presence of a previously overlooked element has often been realized a considerable time before chemical methods were sufficiently advanced for its isolation (e.g. sodium, calcium, lithium, vanadium, fluorine, etc.). On pp. 69, 70, we give a table of the elements (grouped according to the periodic system) showing the circumstances of their discovery, and, when not isolated by their discoverer, of their isolation.

A few isolated points in the history of inorganic compounds remain to be dealt with. The existence of different forms of the same substance (e.g. charcoal, graphite, diamond) has been investigated by many workers since Berzelius characterized such phenomena as a particular form of isomerism. The term "allotropy" was introduced about 1841. It has latterly been realized that such inorganic isomers are probably caused by polymerism (difference in molecular weight) or polymorphism (difference in crystalline form, probably due to difference in molecular structure). Besides oxygen and ozone (Schönbein, 1840), the following cases of elementary allotropy have been studied: sulphur (Mitscherlich, 1852), selenium (Berzelius, 1817; Hittorff, 1851), boron and silicon (Wöhler), tin (Rammelsberg, 1880). There are probably more cases of allotropy in the realm of compounds than of elements, but comparatively few of

Group.	Element.	Atomic Weight (1910).	First Notice of Compounds.		Isolated.	
Ia.	Lithium	7·00	1817	Arfvedson	1855	Bunsen (by electrolysis).
	Sodium	23·00		From very early times	1807	Davy (electrolysis of moist hydroxide).
	Potassium	39·10	1736	Duhamel (distinction from soda)	1807	Davy (electrolysis of moist hydroxide).
	Rubidium	85·45	1861	Bunsen and Kirchhoff (first "new" elements detected by means of the spectroscope)		
	Caesium	132·81	1860			
Ib.	Copper	63·57		From the earliest periods		
	Silver	107·88				
	Gold	197·2				
IIa.	Calcium	40·09		Lime, etc., very early	1808	Davy (from their amalgams, obtained earlier by Seebeck).
	Strontium	87·62	1790	Klaproth and Hope (independently)		
	Barium	137·37	1774	Scheele (distinction from CaO)		
IIb.	Glucinum or Beryllium	9·1	1797	Vauquelin in beryl	1828	Wöhler (action of K on chloride).
	Magnesium	24·32	1695	Crew (Epsom salts)	1808	Davy (as for Ca, Sr, Ba).
	Zinc	65·37		Used very early in alloys		Basil Valentine.
	Cadmium	112·40	1817	Stromeyer		
	Mercury	200·0	300 B.C.	Theophrastus (preparation from cinnabar)		
IIIa.	Scandium	44·1	1879	Nilson (predicted by Mendelejew as "eka-boron")		
IIIb.	Boron	11·0	1702	Homberg (boric acid)	1808	Davy and Gay-Lussac (independently).
	Aluminium	27·1	1754	Marggraf (distinction from CaO)	1827	Wöhler (K on the chloride).
	Gallium	69·9	1875	Lecoq de Boisbaudran (in zinc ores, by the spectroscope; Mendelejew's eka-aluminium)		
	Indium	114·8	1863	Reich and Richter (in zinc blende)		
	Thallium	204·0	1861	Crookes (spectroscopically detected in flue-dust from H_2SO_4 chamber-process)		
IVa.	Titanium	48·1	1791	Gregor	1825	Berzelius (K on fluoride).
	Zirconium	90·6	1789	Klaproth	1824	Berzelius "
	Cerium	140·25	1803	Klaproth, Berzelius		
	Thorium	232·42	1828	Berzelius (oxide ThO_2)	1828	Berzelius.
IVb.	Carbon	12·00		Known from earliest times		
	Silicon	28·3		" "	1810	Berzelius

Group.	Element.	Atomic Weight. (1910).	First Notice of Compounds.	Isolated.
	Germanium	72·5	1886 Winkler (in Freiburg silver ore; Mendelejew's eka-silicon)	
	Tin	119·0	Known to the ancients	
	Lead	207·10	,, ,,	1867 Roscoe.
V*a*.	Vanadium	51·2	1801 del Rio (in lead ores)	
	Columbium or Niobium	93·5	1846 Rose	
	Tantalum	181·0	1801 Hatchett	
V*b*.	Nitrogen	14·01	—	1772 Rutherford.
	Phosphorus	31·0	1669 Brand	
	Arsenic	74·96	Ancient times	13th century alchemists.
	Antimony	120·2	Alchemical times	Basil Valentine.
	Bismuth	208·0	,,	,,
VI*a*.	Chromium	52·0	1797 Vauquelin (in lead ores)	
	Molybdenum	96·0	1778 Scheele, Bergman	1783 Hjelm.
	Tungsten	184·0	1778 ,,	1781 d'Elhujar.
	Uranium	238·5	1798 Klaproth (in pitch blende)	1842 Péligot.
VI*b*.	Oxygen	16·00	—	1774 Priestley, Scheele.
	Sulphur	32·07	Known from earliest times	
	Selenium	79·2	1817 Berzelius	1817 Berzelius.
	Tellurium	127·5	1782 von Reichenstein	1798 Klaproth.
VII*a*.	Manganese	54·93	1772 Scheele	1774 Gahn.
VII*b*.	Fluorine	19·0	1771 Scheele	1886 Moissan (electrolysis of KHF_2).
	Chlorine	35·46	1774 Scheele	
	Bromine	79·92	1826 Balard	
	Iodine	126·92	1811 Courtois	
VIII.	Iron	55·85	Very ancient times	
	Cobalt	58·97	,,	1742 Brandt.
	Nickel	58·68	1751 Cronstedt	
	Ruthenium	101·7	1844 Claus	
	Rhodium	102·9	1804 Wollaston	
	Palladium	106·7	1803 Wollaston	
	Osmium	190·9	1803 Tennant	1859 Deville, Debray.
	Iridium	193·1	1803 Tennant	
	Platinum	195·0	1735 Don Antonio de Ulloa	1750 Watson.

these (e.g. the iodides and sulphides of mercury) have been minutely studied.

The hydrides of the elements form an interesting series; those of the alkaline and alkaline earth metals are of comparatively recent discovery, the rest are mainly non-metallic. The most noteworthy are those of boron (B_3H_3, Ramsay and Hatfield), silicon (SiH_4, Wöhler, 1857; Si_2H_6, Moissan and Smiles, 1902), sulphur (H_2S, Rouelle; H_2S_2, Scheele), and the nitrogen group, which merit special attention:—

NH_3	Ammonia	Compounds known to the ancients; gas discovered by Priestley, 1774.
NH_2OH	Hydroxylamine	Discovered by Lossen, 1865; obtained pure by Lobry de Bruyn and by Crismer, 1891; sulphonic acids studied by Lossen, Divers, etc.
$NH(OH)_2$	Dioxyammonia	In solution only; Angeli, 1907.
N_2H_4	Hydrazine	Discovered by Curtius, 1887; obtained pure by Lobry de Bruyn, 1896.
N_3H	Hydrazoic acid, azo-imide	Discovered by Curtius, 1890; also obtained by W. Wislicenus, 1892.
PH_3	Gaseous phosphoretted hydrogen	Discovered by Gengembre, 1783.
P_2H_4	Liquid phosphoretted hydrogen	,, Thénard, 1845.
AsH_3	Arsine	,, Scheele.
SbH_3	Stibine	,, Soubeiran, 1830.

The oxides and oxy-acids of nitrogen, phosphorus and sulphur are worthy of note:—

N_2O	Nitrous oxide	Davy, 1800 ("laughing gas").
$N_2O_2H_2$	Hyponitrous acid	Divers, 1871; Thiele and Lachmann, 1895; Hantzsch, 1896.
NO	Nitric oxide	Priestley, Dulong, Péligot.
N_2O_3	Nitrogen trioxide	Dulong, 1816; Péligot, 1841.
NO_2	,, peroxide	Dulong, Gay-Lussac.
N_2O_5	,, pentoxide	St. Clare Deville, 1849.
H_3PO_3	Phosphorous acid	Lavoisier; Wurtz, 1849.
$H_4P_2O_6$	Hypophosphorous acid	Salts by Dulong, 1816.
SO_3	Sulphur trioxide	Isolated by Döbereiner.
S_2O_3	Sulphur sesquioxide	,, Weber, 1864.

$H_2S_2O_5$	Thiosulphuric acid	Salts by Gay-Lussac, 1819 ("hyposulphurous acid").
$H_2S(n)O_6$	Polythionic acids ($n = 2$ to 5)	Investigated since 1840 by Wackenroder, Spring, etc.
	Hyposulphurous acid	H_2SO_2, Schützenberger, 1869; $H_2S_2O_4$, Bernthsen, 1900 $H_4S_2O_5$, Bucherer, 1904.

There are also several substances of interest related to hydrogen peroxide :—

O_3	Ozone	Discovered by Schönbein (1840); constitution by Marignac, Andrews and Soret; much used of late in organic chemistry as oxidizing agent.
H_2O_2	Hydrogen peroxide	Discovered by Thénard (1818); anhydrous, Wolffenstein (1894).
S_2O_7	Persulphuric anhydride	Isolated by Berthelot, 1878 (SO_2+O_2 under silent discharge).
$H_2S_2O_8$	Di-persulphuric acid	Only known in dilute solution; $K_2S_2O_8$, electrolysis of $KHSO_4$ (Marshall, 1891).
H_2SO_5	Mono-persulphuric acid	Isolated by H. Caro (1898); used by Baeyer as organic oxidant; $H_4S_2O_9$, Armstrong and Lowry, 1902.
$M^1_2C_2O_6$	Percarbonates	Obtained by electrolysis of $MHCO_3$ (Constan and Hansen, 1897).
$KCrO_5,H_2O_2$	Potassium perchromate	H_2O_2 on chromic acid solution (Barreswil, 1847; Moissan, Berthelot); boric, molybdic, tungstic and uranic acid salts all yield peracids with H_2O_2.

Finally, there are a number of halides of the elements whose discovery presents points of interest :—

BX_3	Boron halides	Investigated mainly by Berzelius, Wöhler and Deville.
SiX_4	Silicon halides	
	Nitrogen chlorides	First studied by Dulong (1812) and then Gattermann.
	Nitrogen iodides	,, Gay-Lussac.

Cl_3	Phosphorus trichloride	First studied by Gay-Lussac (1800).
Cl_5	,, pentachloride	,, Davy (1800).
OCl_3	,, oxychloride	,, Wurtz (1847).
F_5	,, pentafluoride	,, Thorpe (1876).
$AsCl_3$	Arsenic trichloride	,, Glauber.

§ 5. **The Metals of the Rare Earths**—There are a number of rare metals, for the most part occurring together in a few rare minerals of not very wide distribution (chiefly in Scandinavia and Canada), and these are characterized by great similarity in chemical, and in many physical, properties. In some cases chemical reactions do not suffice to effect their separation, which can only be accomplished by fractional crystallization of their salts, the process being controlled by spectroscopic examination.

The following is a list of these elements, taken from the International Atomic Weight table for 1909:—

Element.	*At. Wt.*	*Discovery.*
Scandium	44·1	1879 Nilson.
Yttrium	89·0	1794 Gadolin.
Lanthanum	139·0	1839 Mosander.
Cerium	140·25	1803 Klaproth.
Praseodymium	140·6	1841 Mosander (Didymium).
Neodymium	144·3	1885 Resolved by Welsbach.
Samarium	150·4	1849 Lecoq de Boisbaudran.
Europium	152·0	1896 Demarçay.
Gadolinium	157·3	1889 Lecoq de Boisbaudran.
Terbium	159·2	1843 Mosander.
Dysprosium	162·5	1886 Lecoq de Boisbaudran.
Erbium	167·4	1843 Mosander.
Thulium	168·5	1877 Clève; 1906 Urbain.
Ytterbium	172·0	1878 Marignac.
Lutecium	174·0	1907 Urbain.

As previously remarked, this series is of great theoretical interest, since, as Crookes has shown (1885-9, etc.), it appears to comprise a number of elements which are far more intimately related to each other ("meta-elements," 1889) than is commonly the case, and may therefore throw some more light on the

problem of the genesis of the elements. In the meantime it must be pointed out that scandium, yttrium, lanthanum and perhaps cerium are the only members of the group which readily fall into line with the periodic system; in connexion with this Benedicks (1904) has suggested that the metals with atomic weights intermediate between those of barium and tantalum be interposed as a kind of transitional series between these two. It is noteworthy that this scheme tends to consolidate the periodic table, leaving only eight vacant spaces.

§ 6. **Radio-active Elements**—Since the science of radio-activity came into being search has naturally been made for the elements which give rise most markedly to the phenomenon, and at the present time five such elements, all of them of very high atomic weight, are certainly known, viz. uranium, thorium, radium, polonium and actinium. In 1896 Becquerel noticed the radio-activity of *uranium*, and six or seven years later Madame Curie observed that of *thorium*, and also stated that it was only the product from natural sources (pitch-blende) which showed very marked activity, the effect being much stronger than any observed with pure laboratory uranium or thorium compounds. On the other hand, the latter showed about one hundred times as much radio-activity as any compound of other elements, and it was held to be doubtful whether any other element was at all radio-active.

Mme. Curie, therefore, fractionally analyzed pitch-blende in an attempt to isolate the more radio-active constituents, and found that the radio-activity became concentrated in the barium and bismuth groups. She fractionated the chlorides from the barium precipitates, and finally obtained 0·1 gm. pure *radium chloride* from a ton of pitch-blende. Giesel improved the method of fractionation by using the bromides instead of the chlorides, and so obtained 0·25 gm. pure salt from a ton of mineral. Mme. Curie determined the atomic weight of radium by precipitating the chloride with silver nitrate, and obtained the value 225, agreeing with the place assigned to radium in the

periodic system. Runge and Precht estimated the atomic weight later as 257·8, from spectroscopic calculations, but Mme. Curie's value has been confirmed (1908) by Haitinger and Ulrich, working with larger quantities of radium bromide.

Mme. Curie and Debierne have very recently isolated radium as a white, easily oxidized metal by electrolysis of the fused salts, using a mercury cathode.

Mme. Curie next worked up the precipitates of the bismuth group, and discovered a new element, *polonium*, but did not succeed in isolating a pure salt. Marckwald (1903), however, prepared the element in a state of purity, but only obtained 4 milligrams from two tons of pitch-blende. Polonium was found to resemble tellurium.

Finally, Giesel (1902) and Debierne (1903) discovered an element, similar to thorium or titanium, but more radio-active, which has been named *actinium*.

CHAPTER VI

THE HISTORY OF ORGANIC CHEMISTRY

§ 1. **Organic Chemistry: the Chemistry of Animate Nature**—The knowledge of the laws governing the combination of the chemical elements and the views held at the present day with respect to the final constitution of matter have been mainly derived from inorganic or mineral substances, while the theories of how the atoms are linked together in a compound are based upon what has been discovered during the past century with reference to organic substances, or, in the nomenclature of Lavoisier's time, bodies of animal or vegetable origin. Many simple organic compounds had of course been met with very early in chemical history; marsh gas was known to van Helmont, alcohol (or, *aqua vitae*, as the alchemists thought best to call it), ether and several of the simpler ethyl esters (e.g. "sweet spirits of nitre") were prepared and used medicinally and otherwise much before his time, while quite a number of organic acids (such as acetic, oxalic, benzoic) were known to the alchemists or phlogistonists, and to these Scheele added several more, discovered by him in various plant or animal juices (malic, citric, oxalic, prussic, tartaric, lactic, uric acids). All organic compounds known at the beginning of the nineteenth century were in fact directly obtained from animate nature, and of the more complicated substances a few sugars and plant bases were practically all that were known.

Difficulty was found in accommodating the simple dualistic hypotheses of Lavoisier, Davy, etc., to the cases of such organic

compounds, and many thought that these were part of a distinct realm of chemical nature, subject to different laws. This and the source of all the organic substances then known together led to the idea that such bodies were only formed by the intervention of a special "vital force". This view, which was also suggested by various workers, notably Bergman, in the previous (phlogistic) period, was rendered untenable when it was shown that in several instances pairs of substances of the same empirical composition—one recognized as "inorganic" and the other as "organic" (the terms bearing at that time their literal meaning)—were so closely related that one member could frequently be changed into the other.

The discovery of *isomerism*, indeed, marks the commencement of our modern structural chemistry, and at this point the detailed description of its history must begin.

In 1825 Faraday discovered a hydrocarbon, butylene, of the same percentage composition as Dalton's olefiant gas, and shrewdly predicted that more instances of the kind would follow in connexion with carbon compounds. Somewhat earlier (1823) Liebig and Wöhler proved the existence of two isomeric acids, cyanic and fulminic acids, and in 1828 the latter discovered the famous conversion of ammonium cyanate to urea. Again, in 1832, Liebig and Mitscherlich showed that Berzelius' sarcolactic acid from flesh (1807), and Scheele's lactic acid from sour milk (1780) possessed the same composition, and at about the same time Berzelius isolated racemic acid, of the same composition as Scheele's tartaric acid from argol.

In 1831 Berzelius proposed the term "isomerism" and a year later subdivided it into two new ones, "polymerism" and "metamerism," which in the course of time became changed to "polymerism" (substances of the same empirical but different molecular composition), and "isomerism" (different substances of the same molecular composition).

§ 2. **The Earlier Theories of Structure of Organic Compounds**—To understand the transition from this early

and somewhat chaotic state of affairs to the present tolerably well-ordered system of organic theory, we have to glance at a complicated series of hypotheses designed in succession to explain organic reactions. These may be roughly grouped as follows :—

(1) "Radicle" theories.

(2) "Type" theories.

(3) The modern structural theory, which in some measure combines both the preceding.

Since these temporary hypotheses were devised contemporaneously with the various systems of atomic weights described in Chapter iii. the formulæ used by their authors are very confusing, and so as far as possible the corresponding modern formulæ are added in brackets in the résumé of their work which follows :—

(1) "Radicle" Theories.

Lavoisier's extension of his oxygen theory to include organic acids has already been mentioned; he seems to regard these as oxides of "radicles" containing more than one element, and including in any case carbon and hydrogen. A more precise view of a "compound radicle" was arrived at by Gay-Lussac (1815-22) as the result of his work on the cyanogen compounds, from which it was clear that the cyanogen group functioned as a "compound element" by forming a whole series of compounds, such as cyanogen hydride (HCN), chloride, bromide, iodide, etc. Further support was given to the view that organic chemistry is the "chemistry of compound radicles" by Liebig and Wöhler's investigation of the "radicle of benzoic acid" in 1832. They prepared benzoyl hydride (benzaldehyde), hydrate (the acid), halides, sulphide, ether and other compounds, thus showing that "benzoyl" $C_{14}H_{10}O_2(C_7H_5O)$ behaved in analogous fashion to a simple element. Berzelius strongly supported this *first radicle theory*, since it con-

firmed his own dualistic electrical hypothesis by extending it to organic substances. Several other radicles were investigated in succeeding years, notably cinnamyl (1834, Dumas and Péligot), salicyl (1838, Piria), and cacodyl (1837-43, Bunsen), and the simple theory of organic radicles was generally accepted between the years 1837-40.

Other observations of Gay-Lussac (upon the relations between ethylene, alcohol and ether) led to Dumas and Boullay's *etherin theory*. These authors tried to show in 1828 that ethylene (etherin) performed similar functions to ammonia as a compound radicle, in order to explain (on a "radicle" basis) the connexion between alcohol, ether, and allied compounds; they pushed the analogy too far, however, by suggesting that ethylene was essentially a base like ammonia, and this brought more discredit than was perhaps fair to the original hypothesis, which looked upon alcohol, ether, and ethyl chloride, for instance, as the respective hydrate, oxide, and hydro-chloride of etherin.

In 1834 Liebig and Berzelius parted company to a certain extent with respect to their views on organic structure. Berzelius was always tied down by his dualistic theory, which he seems to have placed before all other considerations. He insisted on regarding all oxygenated compounds as oxides, and so assumed that ether and alcohol were oxides of two different radicles $(C_2H_5)_2$ and C_2H_6. Liebig on the contrary held that these were derivatives of the same radicle "ethyl," but ascribed to "ethyl" double its real molecular weight, whereas Berzelius was correct in this point, as will be seen from the following table :—

Modern.	*Liebig*, 1834.	*Berzelius*, 1833.
Alcohol C_2H_6O	Ethyl oxide hydrate $C_4H_{10}O \cdot H_2O$	$(C_2H_6)O$
Ether $C_4H_{10}O$	Ethyl oxide $C_4H_{10}O$	Ethyl sub-oxide $(C_2H_5)_2O$

Finally, in 1838, Liebig tried to modify still further the conception of the structure of alcohol by taking what he called the "acetyl" radicle $C_4H_6(CH_3C—)$ as his basis. A little consideration will show how this dehydrogenation of the ethyl

group permitted of the oxidation products of alcohol, aldehyde, and acetic acid, being classed as derivatives of the same group as that present in alcohol and ether.

We may therefore sum up the period of "radicle theories" as: (*a*) a general adherence to the view that organic bodies are composed of radicles (groups of atoms) which function as elements and which are in general preserved intact through a whole series of reactions; (*b*) a series of efforts to bring the simple compounds such as alcohol, ether, acetic acid and the like into line with the more distinctive and well-defined radicles such as benzoyl, cacodyl and cyanogen.

(2) "Type" Theories.

The fact which above all others tended to throw doubt upon the radicle theories was the substitution of hydrogen by chlorine in organic compounds. This phenomenon, which was impossible according to the upholders of the dualistic view, was observed by Gay-Lussac, Liebig and Wöhler, Faraday, and Dumas in the respective cases of hydrocyanic acid, benzaldehyde, ethylene and alcohol (to chloral), and in 1834 the last-named worker summed up the facts in his Laws of Substitution (or *metalepsy*, to use his own term). In 1837 Laurent made an attempt, to some extent temporarily successful, to reconcile the radicle theories with the new substitution laws by suggesting that the radicles could be altered to a certain degree by substitution, but that there always remained a *nucleus* (of carbon and hydrogen) which was unalterable.

This satisfied neither Berzelius nor Dumas, although it probably approaches the modern structure theory more nearly than the views adopted by either. A few years later, in 1840, Dumas published a new theory which supplanted the dualistic by a unitary view, each compound being regarded as a complete whole in itself, its components being related in analogous fashion to the worlds of a planetary system. At the same time

he attempted to classify compounds from their reactions according to definite "*mechanical types*" (a method also suggested by Regnault), and further asserted that substances closely related in properties belonged to the same "*chemical type*," general structural similarity without necessarily similar properties being the criterion of inclusion in a given "mechanical type".

An illustration will make this clearer :—

Mechanical type { Alcohol $C_4H_6H_2O_2$ / Acetic acid $C_4H_6H_2O_4$ / Chloracetic acid $C_4Cl_6H_2O_4$ } Chemical type.

Thus there was no definite view held with regard to organic constitution in the beginning of the forties, and as this was also the period (cf. chap. iii. p. 37) when no fixed rule had been adopted by which to determine the true relation between atomic weight and equivalent, there was considerable confusion in almost every department of chemical theory. The criticisms of two French chemists, Laurent and Gerhardt, upon this point almost remind one of the scathing words of Kunkel and Boyle with reference to the charlatan alchemists.

Laurent in 1843 precisely defined the terms atom, molecule, and equivalent, by means of a more rigid application of Avogadro's rule than had hitherto been made.

Gerhardt and Laurent together made it their work to develop the *unitary* view of organic structure, as opposed to the dualism of Berzelius and many of the German chemists. A preliminary to this advance was Gerhardt's "*Theory of Residues*," propounded in 1839. Any organic reaction which can be represented as a binary one, e.g.—

$$C_2H_3OCl + NH_3 = C_2H_3ONH_2 + HCl,$$

must, in order to satisfy the observed differences between ordinary inorganic double decomposition and the reactions of carbon compounds, be explained theoretically on a different basis (for the sake of clearness it may be pointed out that in our time the characteristics of most inorganic double transpositions

are considered to be due to the presence of the reacting substances in the form of ions, the two classes of reactions being thus ionic and non-ionic). Gerhardt's explanation was that in such binary reactions the inorganic parts of the molecules interacted in the ordinary way and the residual (organic) parts then joined to form the new organic substance. A substance so formed was called a "*copulated*" *compound*—formed by the linking together of the two residues. Thus

$$C_2H_3OCl \text{ (Acetyl chloride)} + NH_3 = HCl + \left.\begin{matrix} C_2H_3O \\ NH_2 \end{matrix}\right\} \text{(Acetamide).}$$

He next availed himself of the results furnished by Liebig and Graham respectively on polybasic organic and inorganic acids, and his efforts to explain these in a similar manner led, in 1844, after Laurent's all-important threefold definition recalled above, to a much simplified scheme of atomic and molecular formulæ, and especially to the first systematic classification of organic compounds, carried out jointly by these two workers.

It is interesting to recall that Gerhardt defined organic chemistry as the "*chemistry of the carbon compounds*" rather than of "compound radicles," and that he pointed out the general recurrence of *homologous series* (already hinted at by Schiel (1842) for alcohols and Dumas for acids), and the existence of *isologous series* (the corresponding compounds of similar chemical nature in different homologous series, e.g. alcohol and phenol, propyl alcohol and the cresols) and of *heterologous series* (which are practically the same as Dumas' "mechanical types" (loc. cit.)).

The next definite advance was the evolution of four general types by Gerhardt in 1853, based fundamentally upon hydrogen $\left.\begin{matrix} H \\ H \end{matrix}\right\}$, hydrochloric acid $\left.\begin{matrix} H \\ Cl \end{matrix}\right\}$, water $\left.\begin{matrix} H \\ H \end{matrix}\right\}O$, and ammonia $\left.\begin{matrix} H \\ H \\ H \end{matrix}\right\}N$. (A fifth type, methane $\left.\begin{matrix} H \\ H \\ H \\ H \end{matrix}\right\}C_2(C = 6)$, was afterwards added by Kekulé.)

The events of the intervening nine years between 1844 and 1853 contributed a great deal to this further systematization, and must be briefly summarized.

In the first place, Kolbe and Frankland engaged upon a series of researches in order to modify the old Berzelian theory so as to make it accord with all the new facts then known. In 1845 Kolbe had prepared trichlormethyl sulphonic acid $CCl_3 . SO_3H$, and the corresponding mono- and di-chloro-acids, so that a series of sulphonic acids entirely analogous to the fatty acids from acetic to trichloracetic was formed, and in 1849 Frankland prepared numerous organo-metallic derivatives (from the metals and alkyl iodides) which (by interaction with water) readily yielded substances believed at that time to be the "radicles" themselves; at the same time these chemists jointly investigated the saponification of nitriles to fatty acids and the action of potassium on ethyl cyanide (yielding ethane, but the product was not recognized owing to some experimental error). Finally, in 1850 Kolbe electrolyzed the salts of the series of fatty acids and believed he had isolated the radicles of the acids (in reality, of course, the products were hydrocarbons formed by union of two radicles, e.g.

$$\begin{matrix} CH_3 . COOK \\ CH_3 . COOK \end{matrix} \rightarrow \begin{matrix} \overset{+}{K} \\ K \end{matrix} + \overbrace{2CO_2 + C_2H_6}^{-}).$$

They believed they had thus shown :—

(*a*) the importance of the alkyl radicles in determining the character of a compound (e.g. CH_3-, CH_2Cl-, $CHCl_2-$, CCl_3-).

(*b*) the existence of the radicles themselves.

(*c*) the fatty acids to be "copulated compounds"[1] of oxalic

[1] Kolbe and Frankland used "copulated compound" in the sense given to the term by Berzelius, which differed from that in which it was used by Gerhardt, for Berzelius apparently simply meant that in a "copulated compound" a neutral group was joined to an electro-positive or negative group.

acid and the alkyl radicles (since $(CN)_2 \xrightarrow{H_2O} (COOH)_2$, and $R.CN \xrightarrow{H_2O} R.COOH$).

Much later, in 1857, Kolbe suggested that carbonic acid served as the fundamental type of organic acid, showed how aldehyde, alcohol, and hydrocarbon types could be derived therefrom, and proved there was some truth in his view by predicting the existence and properties of formaldehyde and of secondary and tertiary alcohols, then unknown, but discovered soon after; e.g.

$2HO.(C_2O_2), O_2$	$\left.\begin{matrix}H\\HO\end{matrix}\right\}.(C_2O_2), O_2$	$H.(C_2O_2), H$	$HO.C_2H_3, O$
Carbonic Acid	*Formic Acid*	*Formaldehyde*	*Methylalcohol*
$(HO.CO.OH)$	$(H.CO.OH)$	$(H.CO.H)$	$(HO.CH_3)$

On the other hand, much experimental work was accumulated during this decade which strengthened the "theory of types". The outstanding features are:—

1849	Wurtz.	Formation of amine bases from cyanic esters and ammonia.
1850	Hofmann.	Formation of ammonium or aniline bases from alkyl iodides and ammonia or aniline. (Cf. 1845, Thénard's preparation of analogous phosphine bases.)
1850-52	Williamson.	Preparation of ether from ethyl iodide and potassium ethylate.

The last-mentioned was perhaps the most important of all, for it demonstrated that ether bore the same relation to alcohol as an alkaline oxide to its hydroxide (a connexion previously suggested by Laurent in 1846).

Williamson was thereby enabled on a similar basis to explain the much-discussed mechanism of the preparation of ether from alcohol and sulphuric acid (previously ascribed by Mitscherlich, Berzelius, and others, in default of anything better, to "catalytic action"), and to suggest that alcohols, ethers, acids, and their

derivatives all belonged to one and the same "water type" $\left.\begin{matrix}H\\H\end{matrix}\right\}O$. The preparation of acid anhydrides from acid chlorides and fatty acid sodium salts by Gerhardt, in 1852, came as an excellent confirmation of this theory.

A little later (1854) Williamson and Kay gave a further example of the fruitfulness of this "type" hypothesis by synthesizing the first *dibasic* alcohol—glycol, from ethylene iodide—its existence having become probable, since they had recently prepared orthoformic ester, and Berthelot had just shown glycerol to be tri-basic, these being the first instances of *tri-basic* alcohol derivatives known, thus leaving a gap which was filled by glycol.

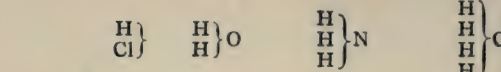
In the meantime it had become customary to refer the ammonium bases of Hofmann and Wurtz to the "ammonia type," and Williamson suggested that combinations of these, yielding "mixed types," occurred in the more complicated compounds. It will be noticed that the term "mixed type" is more or less synonymous with Gerhardt's view of a "copulated compound". For example :—

$\left.\begin{matrix}CH_3CO\\H\end{matrix}\right\}O$	$\left.\begin{matrix}H\\H\\H\end{matrix}\right\}N$	$N\left\{\begin{matrix}H\\H\\CH_2.CO\end{matrix}\right\}O$
Acetic Acid	*Ammonia*	*Amidoacetic Acid*

He also extended the idea to inorganic acids and bases, though not with such great success as on the organic side.

Kekulé's first paper in connexion with organic structure (in 1854) dealt with the extension of Gerhardt's simpler types to an extended series of mixed types.

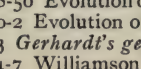
It will be seen that Gerhardt's generalization was a combination of those parts of the older radicle and type theories which had survived the test of application to the numerous new facts discovered between 1830 and 1850, and, further, that the next development (the idea of atomicity or valency) was a very gentle transition from the four main types :—



It will be useful to give a table of the different advances made in each of the two kinds of structure theories :—

Radicle.	*Type.*
1822 "Cyanogen" (Gay-Lussac).	1834 "Laws of Substitution" (Dumas).
1832 "Benzoyl" (Liebig and Wöhler).	1837 Nucleus theory (Laurent).
1832 The older radicle theory (Liebig and Wöhler, Berzelius).	1840 Type theory (Dumas).
1828 Etherin theory (Dumas).	1839 Theory of Residues (Gerhardt).
1834-8 New radicle theory (ethyl and acetyl theories, Liebig).	

1844 Gerhardt and Laurent's classification.
1848-50 Evolution of ammonia type through Wurtz's and Hofmann's work.
1850-2 Evolution of water type through Williamson's work.
1853 *Gerhardt's general type theory.*
1854-7 Williamson's and Kekulé's "mixed types".

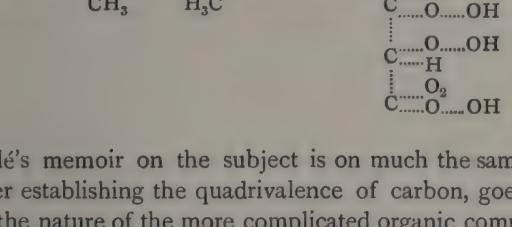
§ 3. **Saturation Capacity and the Modern Structure Theory**—Kekulé saw that the use of "mixed types," such as  implied the presence of polybasic radicles, and in 1857 was able to give definitions of mono- di- and tribasic radicles according to the types in which they occurred.

Several years earlier, however, Frankland reviewed the results of his work on organo-metallic compounds, and on comparing these with inorganic compounds of the same metals, it was seen that each metal possessed a "maximum saturation capacity," i.e. could combine with a certain definite maximum number of monobasic (or to use the clearer term, monatomic) groups, and no more. This observation led in one direction towards the periodic classification of the elements, and in another to the establishment of the valence theory.

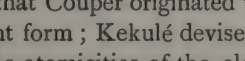
These views upon saturation-capacity, or atomicity or com-

bining power were extended to the case of carbon independently, and almost simultaneously, by Couper and Kekulé in 1858.

Couper showed that carbon possesses four combining units, and elaborated a system of graphic notation of the chief carbon compounds, which is practically that in use at the present day, except that he retained the atomic weight of 8 for oxygen, and, consequently, all his oxygen atoms are doubled. A couple of examples will show the similarity of his formulæ to ours :—



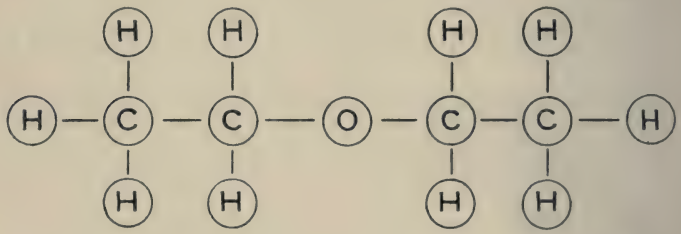
Kekulé's memoir on the subject is on much the same lines, and, after establishing the quadrivalence of carbon, goes on to explain the nature of the more complicated organic compounds, showing how these may be built up of chains of carbon atoms with the other elements attached to the atomic combining units remaining free after two had been used up in the union with neighbouring carbon atoms, e.g. :—



Thus, in about five years after Gerhardt had united all that was best in the radicle and type theories, his efforts had led to the further development which soon ended in the evolution of our present structural ideas.

It has been said that Couper originated the modern structure formula in its present form ; Kekulé devised a system of graphically representing the atomicities of the elements by the size of the symbols, but, like Dalton's system of atom symbols half a

century before, it was found too cumbrous for daily use. Crum Brown introduced the method of representing the graphic formula of a compound, which is next illustrated, in 1865 :—



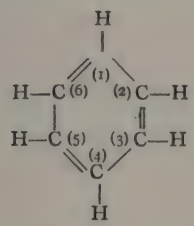
and, by leaving out the circles, Erlenmeyer and Frankland reduced the notation a year or two later to the form it now holds.

§ 4. **Benzene and the Cyclic Compounds**—The reader will have noticed that the compounds whose constitutions were gradually defined by the long succession of hypotheses culminating in the Frankland-Couper-Kekulé valence theory were all of the simplest kind—methane, alcohol, citric acid, oxalic acid, and the like, or, in a word, the "simpler fatty compounds". Groups like benzoyl and cinnamyl and the aniline residue were still written empirically, C_7H_5O, C_9H_7O, C_6H_5N, and so on, and no further insight was gained into their ultimate composition. The benzoyl and cinnamyl radicles were among the first of this class to be discovered, and so, since these were obtained from various "essential oils," their designation (aromatic) became extended to the whole series of bodies chemically related to them.

During the ten years 1858-68, also, much progress was made in extending the classification of fatty compounds and in discovering new compounds and preparative methods based on applications of the valence theory, while the study of the aromatic compounds was always hampered by the ignorance of their

fundamental constitution. It was soon made clear that any theory which would explain the facts must account for the comparative richness in carbon of the aromatic series, for the circumstance that no known aromatic compound contained less than six carbon atoms, reduction of this number leading to loss of the characteristic properties displayed by the series, and for a general resemblance in chemical behaviour running through the whole series and distinguishing it from the fatty compounds.

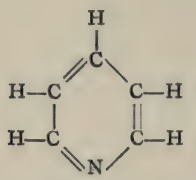
The credit of establishing such a theory belongs in this instance entirely to Kekulé (the valence theory, it will be recalled, was divided between Couper and Kekulé). In 1867 he stated that all the observed facts could be satisfactorily explained by assuming as the characteristic structure of such compounds a nucleus of six carbon atoms united in a ring, each atom having its valencies so disposed as to admit of union with only one monovalent element or group. Benzene, the simplest member (discovered by Faraday in 1825), was therefore formulated as :—



The success of his theory may be best judged by its results : the state of affairs in 1867 has been so materially altered that at the present day more aromatic than fatty substances have probably been synthesized in the laboratory.

The idea of a closed carbon chain was not only applied to the substances then called aromatic, however, but was very soon extended to classes containing elements other than carbon. A commencement was made in 1869, when Körner suggested

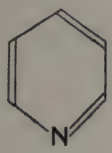
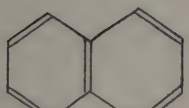
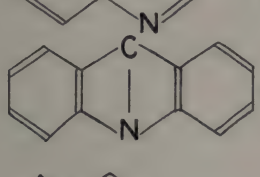
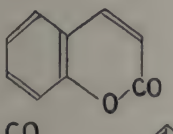
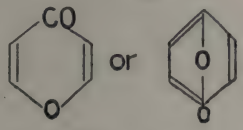
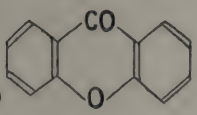
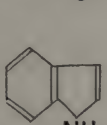
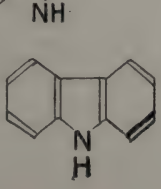
a structure for pyridine on lines analogous to Kekulé's benzene formula :—

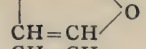
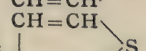
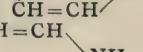
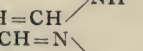
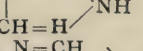
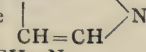
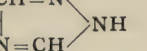
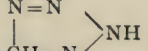
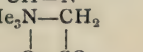
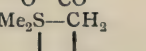
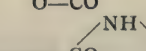
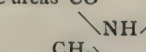


Many other ring-systems, both carbocyclic [1] and heterocyclic, have since been brought into the scheme, and it will probably be simplest to draw up a series of lists illustrating the chief applications of Kekulé's theory to other ring-systems.

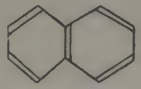
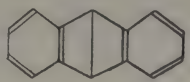
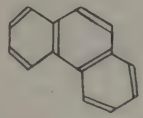
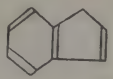
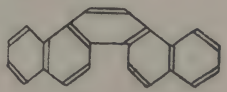
[1] The following terms are now used to define the various classes of organic compounds: *aliphatic*, derived ultimately from the paraffin hydrocarbons; *aromatic*, from the benzene hydrocarbons; *carbocyclic* (homocyclic), possessing a closed chain of carbon atoms; *heterocyclic*, a closed chain including other elements as well as carbon; *homocatenic*, an open chain of carbon atoms; *heterocatenic*, an open chain of carbon and other atoms; *alicyclic*, a fully saturated carbon ring-system (polymethylenes).

(*a*) Heterocyclic Rings analogous to Benzene.

		Proof of Structure.	*Isolation.*
Pyridine		1869 Körner	1846 Anderson; in bon oil.
Quinoline		1871 Dewar 1878 Gräbe	1842 Gerhardt; fro quinine and cinchon
Acridine		1883 Riedel	1871 Gräbe and Caro; synthesiz from diphenylamin
(α-Benzopyrone) Coumarin		1875 Perkin	1875 Perkin's synthes
γ-Pyrone		(Collie, 1899)	1884 Ost.
Xanthones (dibenzo-γ-pyrones)		1881 Merz and Weith	1895 and ff. Occ in nature as dy Kostanecki; synth ses.
Indol		1869 Baeyer and Emmerling	1866 Baeyer; reducti of indigo.
Carbazol		1873 Gräbe	1872 Gräbe; in cru anthracene.

	Furfurane 	1870 Baeyer	1780 Scheele; pyromucic acid. 1831 Döbereiner; furfurol. 1870 Limprecht; furfurane.
	Thiophene 	1883 V. Meyer	1883 V. Meyer; in coal-tar benzene.
	Pyrrol 	1870 Baeyer	1834 Runge; in coal-tar. 1858 Anderson; prepared pure pyrrol.
	Pyrazole 	1887 Knorr	1887 Knorr; first derivatives. 1889 Buchner.
	Glyoxaline 	1877 Ladenburg 1883 Japp	1856 Debus; from alcohol and HNO_3.
	Triazole 	1889 Andreocci	1892 Andreocci; condensation of acid amides with acid hydrazides.
	Tetrazole 	1885 Bladin	1892 Bladin; synthetically.
IV.	Betaïne 	1870 Liebreich	1866 Scheibler; in beet-juice
	Thetine 	1878 Crum Brown and Letts	1874 Crum Brown and Letts.
	Alkylidene ureas 	1879 Rudolph	1891 Hemmelmayer.
III.	Ethylene oxide 	1859 Würtz	1859 Wurtz; from ethylene chlorhydrin.
	Diazomethane 	1894 V. Pechmann	1894 V. Pechmann; action of alkalies on nitrosamines.

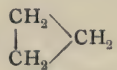
(*c*) Conjugated Carbocyclic Compounds.

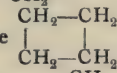
		Proof of Structure.	*Isolation.*
Naphthalene		1866 Erlenmeyer, sen.	1819 Garden; in coal-tar.
Anthracene		1870 Gräbe and Liebermann	1832 Dumas and Laurent; in coal-tar.
Phenanthrene		1870 Gräbe and Liebermann	1873 { Fittig / Gräbe } independently.
Indene		1884 Baeyer and W. H. Perkin, jun.	1890 Krämer and Spilker; from coal-tar.
Fluorene		{ 1874 Gräbe / 1878 Fittig }	1867 Berthelot; pyro-synthesis.
Chrysene		1895 Bamberger	1837 Laurent; in coal-tar.

(*d*) Reduced Carbocyclic Compounds.

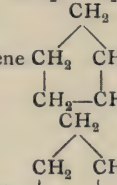
The cyclic polymethylenes have been prepared from the second to the eighth member, interest in this class having been aroused by Baeyer about 1881. The series is interesting since it forms a kind of intermediate stage between the paraffins (non-cyclic, saturated) and the aromatic hydrocarbons (cyclic, unsaturated). Further, it has contributed to our knowledge of the steric conditions of the carbon atom, for in 1885 Baeyer showed that according to van 't Hoff's theory of the distribution of the four carbon affinities in space (see § 7) the five- and six-membered rings should be formed most easily and be the most stable, since in these positions the directions of the valencies suffered least distortion when forming the closed system (Baeyer's *Strain theory*).

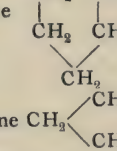
The parent hydrocarbons were obtained by the following workers:—

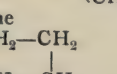
Cyclo-propane, trimethylene  1882 Freund.

Cyclo-butane, tetramethylene  1894 W. H. Perkin, jun. (only the chloro- oxy- and amido-tetramethylenes).

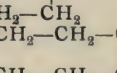
1907 Cyclobutane: Willstätter & Bruce.

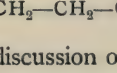
Cyclo-pentane, pentamethylene  1893 J. Wislicenus.

Cyclo-hexane, hexamethylene  1894 Baeyer.

Cyclo-heptane, heptamethylene  1893 Markownikow.

Cyclo-octane) cyclo-octadiene 1903 Ciamician and Silber.

Cyc'o-octane  1907 Willstätter and Veraguth.

Cyclo-nonane  1907 Zelinsky.

Returning to the discussion of a formula for benzene, upon which all the other ring-formulæ may be said to depend, it will

be obvious that a considerable amount of laborious confirmatory work was necessary in order to prove beyond all doubt that benzene really possessed the structure assigned to it by Kekulé. This has been conscientiously carried out by a number of workers at different periods, and its nature will best be grasped by discussing it in the order of the problems which presented themselves for solution.

(*a*) The formula postulates a perfectly symmetrical structure for benzene.

This, or in other words, the equivalence of the hydrogen atoms in benzene has been proved by Ladenburg (1874), Wroblewski (1872-8), and others by replacing all the different hydrogen atoms in turn by the same group, the same product being invariably obtained.

(*b*) It demands the presence of a closed chain of carbon atoms.

The proof of the ring-structure was really completed by W. H. Perkin, jun. (1891-4) when he synthesized various derivatives of hexahydrobenzene as well as the hydrocarbon itself, and obtained products identical with those obtained by reduction of the benzene molecule (Baeyer, 1887-92).

(*c*) It suggests the existence of one mono-substitution-product, three[1] di- and three tri-substitution products of benzene by one kind of group.

This problem, "orientation," was one of the most troublesome to solve, and some years elapsed before definite proof was forthcoming that the theory was here in full accordance with the facts. The main factors contributing to the final satisfactory proof were as follows :—

1871. Baeyer showed that phthalic acid (from naphthalene by oxidation) is *ortho*-(1, 2)-dicarboxyl-benzene, and that isophthalic acid (from iso-xylene, produced in turn from mesitylene) is *meta*-(1, 3)-dicarboxyl-benzene, so that terephalic acid must be the *para*-(1, 4)-compound.

1874. Körner showed that an *ortho*-di-substitution product should yield two, a *meta*- three, and a *para*- only one tri-substitution product, and on this basis determined the orientation of the three known dibromobenzenes.

[1] Excluding the possible second diortho-substituted substances, referred to later.

1872. Griess proved that of the six known diamino-benzoic acids, two gave one diamino body, three gave another, and one another. Arguing conversely to Körner, he arrived at the same conclusion respecting the orientation of the di-substitution products.

1875. Ladenburg, by a complicated process, gave definite evidence that mesitylene was 1, 3, 5 trimethylbenzene, thereby confirming Baeyer's deductions regarding isophthalic acid.

These combined proofs put the practical utility of Kekulé's theory beyond all doubt, but there has always been one uncertain point with reference to it, namely, the disposal of the fourth valency of each combination. Kekulé represented these as forming three pairs of ethylenic bonds, but the stability and general chemical behaviour of aromatic derivatives are entirely opposed to such an accumulation of ordinary fatty "unsaturated linkings". Between 1887 and 1892 Baeyer carried out an enormous series of experiments on the reduction of various carboxylic acids of benzene, with a view to clearing up this point, but, although numerous important observations were made in various directions, the main object of the inquiry was not attained.

Another line of attack was the physical properties of benzene. We shall see in Chap. x. (p. 181) how the numerical values of various physical properties are sometimes adapted for showing the constitution of a substance. It is possible in this way to calculate different values for benzene according to different formulæ which it may possess, and to compare these values with that found for a given property by experiment. This has been done by Schiff (1883) and Horstmann (1887) with molecular volume, by Brühl (1894) with refractive index, and by Thomsen (1880), and Stohmann (1893) with reference to heats of combustion of benzene and various derivatives, but the results are conflicting and do not all point to the same formula.

A property which seems to shed a little more light on the problem is the absorption spectrum of benzene, studied by Baly and Collie, and by Hartley, and referred to again later in this paragraph.

Numerous formulæ have from time to time been proposed in order to account for the remaining valencies of the carbon atoms. These can be divided into two classes, *static* and *dynamic*, according as the component atoms are conceived in a state of rest or motion.

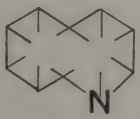
The "*diagonal*" formula was the first of the former type, and was suggested by Claus in 1867.

It bears an apparent resemblance to the Armstrong-Baeyer "*centric*" formula (1892), which supposes the extra valencies to be directed to the centre of the benzene nucleus, so as mutually to satisfy each other. (In 1869 Ladenburg put forward his "*prism*" formula, which was later refuted, chiefly owing to Baeyer's work on the reduced benzoic acids.)

The Armstrong-Baeyer conception of the benzene molecule was extended by Bamberger to numerous six-membered rings, both carbo- and hetero-cyclic. He succeeded in explaining by its means certain characteristic reactions of "conjugated aromatic nuclei," such as those in the

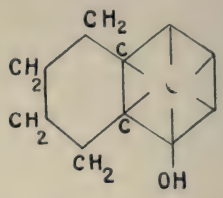
napthalene

anthracene and

quinoline  series,

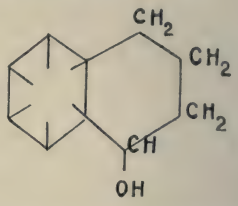
especially showing why reduction products such as, e.g. :—

(ar)-tetrahydro-α-naphthol



should behave as aromatic substances while those like

(ac)-tetrahydro-α-naphthol



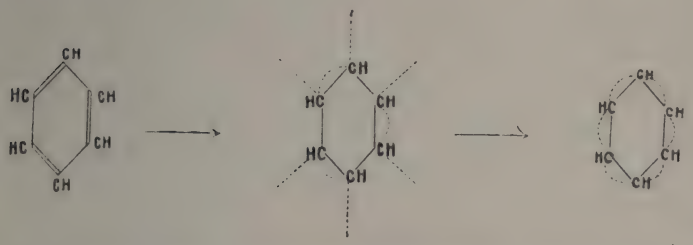
resemble the fatty series more nearly in chemical behaviour.

No one believes at the present time that the atoms in any compound are at rest, i.e. always remain in the same relative positions, and, therefore, it is more interesting to review the attempts made to account for the constitution of benzene on dynamical grounds. Kekulé himself saw that, in addition to the questionable existence of "double bonds" in benzene, his original formula involved the possibility of two ortho-di-substitution products if the substituting groups were not the same. He, therefore, suggested (in 1872) that the fourth valency oscillated between the carbon atoms, thus :—

Knorr, in 1894, owing to his experiments on methyl pyrazole (cf. § 5), assumed that the hydrogen atoms, rather than the carbon linkings, were in a state of oscillation.[1]

[1] It may be remarked that in a few instances such isomeric diortho compounds have been obtained, e.g. two o-nitrotoluenes. The differences

On the other hand, Thiele arrived at quite a different formula in 1899, based on his theory of "partial valencies" (chap. iv., p. 54). Starting from Kekulé's formula, he obtained the new formula for benzene as follows :—



The most comprehensive formula of benzene is that proposed by Collie in 1897. He assumes that each carbon atom is vibrating, and that consequently the relative positions of the atoms are always altering. In this way the molecule passes and repasses through a series of phases, isolated phases being represented, as a matter of fact, by formulæ such as Kekulé's and the centric arrangement. An interesting point is that in this system there are seven possible ways of making and breaking the "linkings" of the carbon atoms during a complete vibration, and these may possibly give rise to the seven "absorption bands" in the ultra-violet spectrum of benzene. It should be observed that Collie's formula is steric, i.e. it pictures other atoms as they are arranged in space, not simply as a plane projection of the spacial configuration.

Other steric but static benzene formulæ (all based upon van 't Hoff's conception of the carbon atom as acting at the centre of a regular tetrahedron, with its valencies directed towards the apices) had been previously put forward, notably by

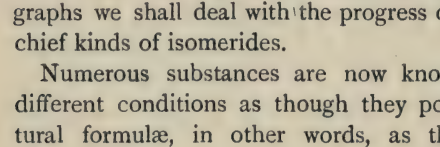
between the two forms are very slight, and lie entirely in physical properties (Knoevenagel). The phenomenon has been termed "moto-isomerism".

Baeyer (1888) and Vaubel (1891), whose attempts, however, do not satisfactorily account for the phenomena shown on reduction of the benzene nucleus by hydrogen. Sachse (1890) represented the most stable and symmetrical grouping of the atoms by six tetrahedra superposed upon six faces of a regular octahedron, leaving two parallel faces vacant. Both Thiele and Brühl supported Sachse's view.

The whole position may be summed up by saying that at present Collie's formula offers the most satisfactory theoretical explanation of the variety of experimental data, while for ordinary practical purposes Kekulé's original "hexagon" still suffices.

§ 5. **Dynamic Isomerism**—The most interesting developments of organic theory during recent years have centred round isomerism of one kind or another, and in the following paragraphs we shall deal with the progress of our knowledge of the chief kinds of isomerides.

Numerous substances are now known which react under different conditions as though they possessed different structural formulæ, in other words, as though the same substance combined in itself the properties of two isomeric compounds. A notable early example was that of isatin



(labile) or

(stable) (Baeyer, 1883); two years later Laar called attention to other instances (nitrosophenol, acetoacetic ester, etc.) and suggested for the phenomenon the name tautomerism.

Isomerism of this type has probably been more discussed in the case of acetoacetic ester than of any other single substance. This body was discovered in 1863 by Geuther, who formulated it as $CH_3 . C(OH) : CH . COOC_2H_5$, while Frankland believed it to be ketonic, $CH_3 . CO . CH_2 . COOC_2H_5$.

Both the mechanism of its formation and its chemical properties have furnished difficulties; the latter tend to show that it reacts sometimes in the hydroxylic and sometimes in the ketonic form. As these two forms are characteristic of the tautomerism displayed by many compounds, a convenient nomenclature was suggested for them by Brühl in 1893, viz. the *enol-* (hydroxylic) and *keto-* (ketonic) forms.

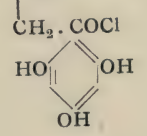
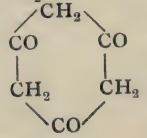
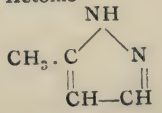
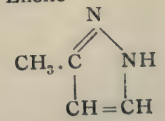
A historical survey of tautomerism must include an account of the chief tautomers discovered, of the methods applied in their investigation, and of the theories put forward to explain the mechanism of the changes involved.

The chief examples of tautomeric substances so far known are included in the following summary; those discovered before the advent of modern structural views were, needless to say, only realized to be desmotropic (to use an equivalent term coined by Jacobson in 1887) at a much later date.

The summary may conveniently be divided into the two main kinds of tautomers:—

(*a*) Substances reacting in two forms, but only isolable in one.

(*b*) Substances reacting in two forms, both of which can be isolated.

(*a*)	*"Stable" Form Discovered.*		*Alternative "Labile" Possibility Suggested.*	
Cyanuric acid	Enolic	ca. 1780 Scheele	Ketonic	1885 Hofmann.
Acetaldehyde	$CH_3.CHO$	1774 Scheele	$CH_2:CH(OH)$	1878 Erlenmeyer.
Cyanamide	$CN.NH_2$	1838 Bineau	$HN:C:NH$	1875 Weith.
Succinyl dichloride	$CH_2.COCl$ | $CH_2.COCl$	1853 Gerhardt	$CH_2.CCl_2$ | $CH_2.CO$ >O [1]	1883 Gräbe.
Phloroglucinol		1855 Hlasiwitz		1885 Baeyer.
Succino-succinic ester	Ketonic	1882 Herrmann	Enolic	1886 Baeyer.
Methyl-pyrazole		1894 Knorr		1894 Knorr.
Camphor	Ketonic	In remote times	Enolic	1888 Cazeneuve. 1901 Forster.
Amides	$R.CO.NH_2$	1832 Liebig and Wöhler	$R.C(OH):NH$	1877 Pinner.
Sulphinic acids	$R.SO.OH$	1857 Hobson	$R.SO_2.H$	1880 Otto.

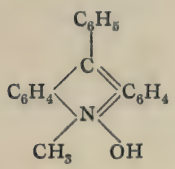
[1] This is now generally regarded as the stable form.

(*b*)	*Different Forms Isolated.*	*Chief Worker.*
Tribenzoylmethane	One enol and one keto	1893 Claisen.
Mesityloxideoxalic ester	„	1896 Claisen.
Phenylnitromethane	Hydroxylic (acid) and non-hydroxylic (ψ-acid)	1896 Hantzsch.
Formylphenylacetic ester	One enol and one keto	1896 W. Wislicenus.
Dibenzoylsuccinic ester	Various di-keto, keto-enol and di-enol forms	1896 Knorr.
Diacetylsuccinic ester	Various di-keto, keto-enol and di-enol forms	1896 Knorr.
Benzylidene diacetylacetone	Various di-keto, keto-enol and di-enol forms	1899 Schiff.
Camphor-quinone phenyl-hydrazone	Normal hydrazone and oxy-azo forms	1899 Betti.

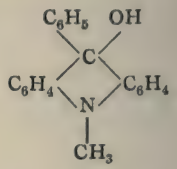
Arguments based upon both chemical and physical properties have naturally been used in attacking the problem, but the bulk of those derived from chemical changes have been proved within the last ten or twenty years to be invalid, since the different reagents used were shown to have first produced a particular isomer, which then entered into the reaction. Thus some reagents furnish the keto-, others the enol-isomer; some exert a *ketonizing*, others an *enolizing*, effect. For this reason, all acidic or alkaline reagents have been banned, and chemists have found very few suitable reagents for tautomeric investigation by chemical means; Schiff (1898) used benzalaniline, which unites with either enol- or keto-acetoacetic ester, yielding entirely different products. Phenyl isocyanate has been used to detect hydroxyl or amino groups in desmotropic compounds, and sometimes alcoholic ferric chloride will show the presence of an enol-form without disturbing the constitution of the isomer (W. Wislicenus, 1896).

Study of the physical properties has naturally often proved much more successful; differences in the values of different forms of keto-enol isomers were found by W. H. Perkin, sen. (1892) for magnetic rotation, Traube (1896) for molecular volume, and Brühl (1899) for refractive and dispersive power. Hantzsch traced the change of *acids* (R.CH:NO.OH)

to *pseudo-acids* ($R.CH_2.NO_2$), and of *ammonium bases*



to *ψ-ammonium bases*



by electrical conductivity measurements in 1896, and in the same year Wislicenus followed the keto- $\rightleftarrows$ enol change by a colorimetric method based upon the intensity of colour furnished by a standard alcoholic ferric chloride solution. Similarly, solubility and melting-point curves have been studied by Lowry (1904), Knorr and others, while Hartley and others have examined the absorption spectra of tautomeric compounds. Another property which is especially delicate when it can be applied is alteration in optical activity or *mutarotation*, as Lowry has termed it; he has applied the method to the isomerism of nitro- and bromo-camphor and of α- and γ-glucose.

The theories of tautomeric change are chiefly associated with the names of Butlerow (1877), Laar (1885), Knorr (1894-99), Lapworth (1902), and Lowry (1904). Laar held the phenomenon to be due to the rapid oscillation of particular linkings in the molecule, his explanation being thus *intramolecular*. Knorr, on the other hand, considered the process to be *intermolecular*, molecules of either isomer being present, but continually changing into the alternate form; for instance, with methylpyrazole (1894) obtained from two isomeric phenyl methylpyrazoles:—

In other words, the hydrogen atom oscillates, rather than the double linkings. In 1899 he stated further that tautomers tend in general to form an equilibrium ("allelotropic") mixture of

constant composition, the examples where only one form is known being limiting cases of this rule. He had also, four years earlier, expressed the conviction that the isomerizing effects produced by different reagents were really due to the action of ions, and in 1902 Lapworth removed various discrepancies which occur if ordinary acid or alkaline ions are assumed to produce the effect by suggesting the changes were essentially caused only by the action of organic ions.

Lowry in 1904 introduced the term *dynamic isomerism* to embrace all the forms of isomerism previously classed as tautomerism, desmotropism, etc. He showed that tautomeric changes could be treated mathematically by the law of mass action, just like ordinary chemical "reactions of the first order," the velocity constants for typical cases having been previously worked out by himself in 1899 (optical activity of camphor derivatives) and by Küster (1895). He assumed, too, that the mechanism of the change was a catalytic action due to the presence of ions.

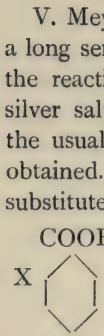
Finally, in 1904-5, Baly and Desch put forward an explanation, different from any of the above. Since simple hydroxylic or ketonic substances show no "absorption band" in the ultra-violet spectrum, while keto-enolic dynamic isomers usually possess one, they considered that the alteration $\rangle C=O \rightarrow =\overset{|}{C}-OH$ is responsible for the production of the band, i.e. tautomerism phenomena are due to vibrations in the molecule caused by the constant structural alteration.

§ 6. **Steric Hindrance**—A problem not unconnected with those reviewed in the two preceding sections is that known latterly as "steric hindrance". From time to time exceptions have been found to reactions which generally take a well-defined course, and in many cases it has seemed probable that the cause of the anomaly is the near presence of other non-reacting groups in the molecule which, apparently, protect the reacting radicle from attack by reason of their bulk. Victor Meyer was

the main author of this theory of *steric hindrance*, which dates from about 1894. The chief examples noticed previous to his work are :—

1872	Hofmann	Substituted anilines such as $C_6(CH_3)_5NH_2$, do not yield quaternary ammonium iodides of the type $R.NR_3I$.
1883-84	,,	The nitrile group of certain highly substituted benzonitriles could not be saponified in the usual way.
1891-92	Claus	Noticed that the di-ortho-substituted cyanides were especially hard to saponify, but that the nature of the substituent also modified the reaction.
1890	Pinner	Ortho-substituted cyanides do not readily give imino-ethers $R.C\begin{matrix}=NH\\ \diagdown OEt\end{matrix}$
1890	Kehrmann	Ortho-substituted quinones do not readily give oximes.
1891	V. Meyer	,, ,, ,, ,, hydrazones.

V. Meyer was thus led to examine the rates of esterification of a long series of substituted benzoic acids, and found that while the reaction proceeded equally well on the whole when the silver salt of the acid was heated with ethyl iodide, yet by the usual hydrochloric acid method very varying results were obtained. These led to his "Esterification Law". In the substituted benzoic acids, the presence in the ortho-position



to the carboxyl group of a radicle of low molecular weight retards esterification, while groups of higher molecular weight may altogether prevent it.

In 1899 the extension of Meyer's researches to the substituted fatty acids was undertaken by Sudborough, showing that substituents in the methylene group next to the carboxyl behave in the same manner as ortho-substituents in benzoic acid, while in 1895 and 1897 Meyer and Kellas respectively showed that those esters which are formed with difficulty are also the hardest

to hydrolyze, showing clearly the "protecting" influence of the adjacent radicle.

Other instances of steric hindrance occur in Bischoff's investigations as to the conditions which influence chain-formation in the malonic and aceto-acetic ester syntheses (1880-8); Schryver (1899) showed that the sodium salts of ortho- and para-nitrophenols, and di-ortho-bromophenols do not give the general reaction with camphoric anhydride, forming aryl hydrogen camphorates.

The fact that other influences besides the size of the molecule may sometimes partially or completely mask the hindering effect is shown by the rates of reaction of sodium hydrogen sulphite with various substituted ketones (Stewart, 1905), and by the sulphination of a series of phenolic ethers :—

$$R.C_6H_4.OEt \rightarrow R.C_6H_3(OEt)(SO_3H) \rightarrow [R.C_6H_3(OEt)]_2SO \rightarrow [R.C_6H_2(OEt)]_3S.OH.$$

The stage to which the latter reaction proceeds is found to depend upon :—

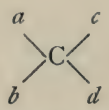
(*a*) The steric hindrance due to the presence of ortho-substituents.

(*b*) The directing influence of the alkoxyl (OEt) group (Smiles and Le Rossignol, 1908).

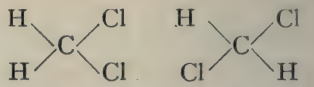
§ 7. **Stereo-isomerism** (*a*) **Geometrical Isomerism**—There are two other kinds of isomerism remaining, which have been explained by considerations of the arrangement of the groups in space about the central carbon atoms of the organic molecule. The first which will be discussed is that which manifests itself most markedly in chemical properties; the second, which has been known for a much longer period than the first, is an isomerism embracing three (or four) isomers in each instance, which in general differ mainly in their effect upon polarized light. In either case we must first recapitulate the views adopted as to the nature of the carbon atom before the development of the theories of geometrical and optical isomers can be understood.

Kekulé's views of organic structure were based upon the quadrivalency of carbon; the disposition of the valencies in space was not considered. As we have seen, his theories, especially that dealing with benzenoid compounds, cleared up the constitution of multitudes of compounds, but still there remained cases of isomers which were unaccounted for, such as that existing between maleic and fumaric acids or between the four tartaric acids.

Van 't Hoff set out in 1874 to try to solve the problem by obtaining an idea of the arrangement of the groups about a carbon atom. Starting from the known fact of the equivalence of the hydrogen atoms in methane he argued that the disposition of groups must be either :—

(*a*) A plane arrangement, such as 

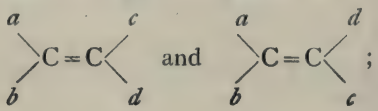
(*b*) A space arrangement whereby the affinities would be inclined equally to one another and directed towards the carbon atom (the familiar tetrahedron).

Since (*a*) involves isomerism of substances, e.g. 

such as is contrary to observed fact, the alternative (*b*) must be taken.

Le Bel introduced practically the same view of the carbon atom at the same time, but independently of van 't Hoff.

According to this view the atoms of substances containing an ethylenic bond would be so arranged in space that the four remaining groups would all lie in one plane, and as the double linking would prevent free rotation of the central carbon atoms, geometrical isomerism might be expected :—



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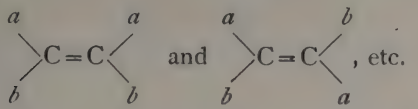
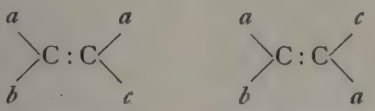


During the next ten years J. Wislicenus examined many cases of such geometrical isomerism in ethylenic compounds and published his results, "Die räumliche Anordnung der Atome," in 1887. The isomers used were maleic and fumaric, crotonic and iso-crotonic, citraconic and mesaconic, oleic and elaïdic acids, etc., stilbenes ($C_6H_5 . CH : CH . C_6H_5$), tolanedihalides ($C_6H_5 . CX : CX . C_6H_5$), and many others.

In 1892 Baeyer introduced convenient terms for the two kinds of isomers, viz. :—



Cis-compound. *Trans-compound.*

In the preceding years he had prepared a series of similar isomers in the case of some of his reduced aromatic acids.

The "configuration" (cis- or trans-) of the isomers was based by J. Wislicenus chiefly on the ability to yield anhydrides or cyclic compounds, and the formation from the corresponding acetylene derivative in the case of cis-compounds, while superior stability and characteristic physical properties served to point out the trans-compounds.

Some other cases of geometrical isomerism must be briefly referred to :—

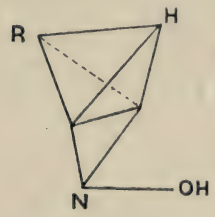
(*a*) *Stereo-isomeric Oximes*, $\begin{matrix} R_1 \\ R_2 \end{matrix} > C : N . OH.$ — In 1883 V. Meyer and Goldschmidt obtained two benzildioximes, $C_6H_5 . C(: NOH) . C(: N . OH) . C_6H_5$, and five years later V. Meyer and Auwers also prepared two benzilmonoximes, a third dioxime being added in 1889. Their explanation of

the isomerism was soon seen to be faulty; meanwhile Beckmann had obtained two benzaldoximes, which he formulated as

(*a*) C_6H_5 CH = N . OH and (*β*) $C_6H_5 . CH . NH$ (O), a view which

was speedily disproved by Goldschmidt.

In 1890 Hantzsch and Werner put forward their theory, which is simply an extension of van 't Hoff's views to the —CH : N— system, based on the assumption that the three nitrogen valencies are directed to the apex of a regular tetrahedron, so that, for instance, R . CH : N . OH may be spacially represented as :—



This represents the isomerism as similar to the . CH : CH . cases, and the chemical and physical characteristics of the isomeric oximes quite agree with this view, while, further, the isomerism appears and vanishes in accordance with the theory. In cases where only one oxime is known it is assumed that one of the radicles has a pre-eminently strong attraction for the hydroxyl group.

The configuration of these isomers (termed *syn-* and *anti-* by Hantzsch, previously to Baeyer's *cis-* and *trans-*) has been determined by :—

(i) Ready conversion of one (the *syn-*) form to a nitrile by loss of H_2O.

(ii) The "Beckmann change," which takes place as follows in presence of PCl_5 or HCl and H_2SO_4 :—

$$a.C.b \;\Vert\; N.OH \quad \left(a.C.OH \;\Vert\; N.b\right) \rightarrow a.CO \;|\; NH.b;$$

$$a.C.b \;\Vert\; HO.N \rightarrow \left(HO.C.b \;\Vert\; a.N\right) \rightarrow CO.b \;|\; NH.a.$$

(iii) Patterson and McMillan (1908) have followed the con-

version of labile into stable isomeric oximes dissolved in ethyl-tartrate by means of the varying rotating power of the solvent.

(*b*) *Stereo-isomeric Benzhydroximic Ethers* $\begin{matrix} C_6H_5 \\ EtO \end{matrix}\!\!>\!C : N . OH.$

—These, observed by Lossen in 1872, have been explained by Werner (1892-6) on the Hantzsch-Werner hypothesis.

(*c*) *Stereo-isomeric Hydrazones* (Hantzsch, 1890) and *osazones* (Anschütz, 1895) have also been noticed.

(*d*) *Isomeric Diazo-compounds.*—In 1863 Griess discovered the diazo-compounds and isolated potassium benzene diazotate, $C_6H_5N_2OK$. In 1894 Schraube and Schmidt obtained a second potassium salt by using different experimental conditions. Hantzsch forthwith assumed the differences to be due to geometrical isomerism, viz. :—

$$\begin{matrix} C_6H_5 . N \\ \| \\ KO . N \end{matrix} \quad \text{and} \quad \begin{matrix} C_6H_5 . N \\ \| \\ N . OK. \end{matrix}$$

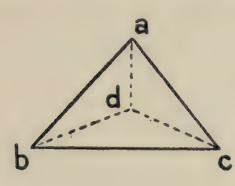
The previous formulæ for diazo-bodies were Kekulé's azo-formula, $C_6H_5 . N : N . X$ (1867), and Blomstrand's diazonium formula, $\begin{matrix} C_6H_5 \\ X \end{matrix}\!\!>\!N : N$ (1875), and to these two Bamberger referred the isomeric diazotates. There ensued a protracted controversy between Hantzsch and Bamberger, in the course of which other isomeric diazo bodies (diazosulphates and cyanides) were obtained.

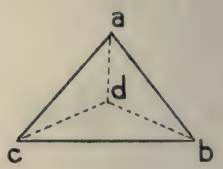
Finally, it was generally admitted that both views were probably correct; while the Blomstrand formula probably better expresses the constitution of the salts of strong acids, the isomerism of derivatives of weaker acids is to be explained upon a stereo-chemical basis.

§ 8. **Stereo-isomerism** : (*b*) **Optical Isomerism**—In 1815 Biot noticed that sugar solutions rotate the plane of polarized light, a phenomenon previously observed in quartz by Arago (1811). In 1819 he showed that a substance which is thus

"optically active" in the liquid remains so in the gaseous state. In 1820 Herschel pointed out that it was enantiomorphous (quartz) crystals which deviated polarized light, and Pasteur, thirty years later, found that sodium ammonium tartrate crystals were also enantiomorphous (i.e. possessed forms which were mirror images of each other), the two kinds of crystals moreover yielding respectively dextro- and laevo-tartaric acids. Pasteur suggested that the mutual cause of the hemihedral crystals and of the optical activity lay in some asymmetry of the atomic structure. Finally, in 1873, J. Wislicenus showed that the isomerism of the lactic acids from flesh and from sour milk (cf. p. 77) also manifested itself by the optical activity of one form, and stated that the cause must be connected with the spacial disposal of the atoms.

Then, in 1874, came the Le Bel-van 't Hoff theory of the spacial arrangement of atoms, which accounted for the existence of more than one derivative of substances containing an "asymmetric carbon atom".





It may be said that all optically active compounds have been found to possess asymmetry of this nature, although the converse is not yet experimentally true in some cases. Such compounds have been known for so long and are so numerous that examples are superfluous. The number of isomers of a compound containing one asymmetric atom is in general three —a dextro-, laevo- and racemic isomer; the two former are alike in all properties but rotating power, in which they are opposite; the latter usually varies somewhat in physical properties from the optically active compounds. A fourth stereo-isomer of

tartaric acid, *meso-tartaric acid*, was discovered by Pasteur and explained by van 't Hoff as a compound in which the rotation of one-half of the molecule was compensated by that of the other half. The justice of this view was proved in 1892 when E. Fischer reduced mucic acid $COOH[CH_2OH]_4COOH$ (another *meso* compound) to galactonic acid $CH_2OH[CH.OH]_4COOH$, which being no longer an internally-compensated, but rather an externally-compensated (racemic) molecule, was successfully split up into active isomers. The meso isomers possess well-marked physical differences from the other forms.

The correctness of Kekulé's benzene theory has often been tested by attempting to obtain optically active forms of the benzene molecule. Such experiments (Le Bel, 1882; Lewkowitsch, 1888; V. Meyer and Lühn, 1895) have always, by their failure, afforded good negative proof of Kekulé's views.

A curious anomaly found in optical activity is that known as the *Walden inversion;* an active compound usually yields by chemical change a new active compound of the same general sign, but Walden (1895) found that *d*-malic acid yielded *l*-chlorosuccinic acid with PCl_5, while the latter gave *l*-malic acid or *d*-malic acid according as silver or potassium hydroxides were used to remove the halogen. Other similar instances have been discovered (Purdie, 1895).

Quantitative Theories of Optical Activity.—In 1890 the idea of a *molecular asymmetry-product*, the value of which was conceived possibly to be parallel with the degree of optical activity, was evolved independently by Crum Brown and by Guye. Crum Brown assumed that each attached group exercised an influence K_1, K_2, K_3, K_4, in the asymmetric carbon atom, the differences between K_1, K_2, K_3, K_4, giving the rotatory power.

Guye's hypothesis is similar, except that he considers the mass of the groups to be the "influence". This theory has proved in accordance with facts in a number of series and at variance with facts in many others. Groups of equal mass should destroy activity were mass the only influence, but Guye

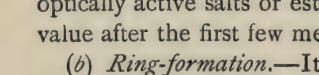
himself, Purdie, Walden and others have shown that compounds containing two different groups of equal mass are optically active. It may be remarked that this discrepancy would disappear if the "influences" were assumed to be forces of some kind between the groups and the asymmetric atoms. All researches carried out on the quantitative nature of optical activity tend to show it to be, of all physical properties, that most susceptible to constitutive influences.

(*a*) *Asymmetric Synthesis.*—Cohen and Whiteley (1901) made several unsuccessful attempts to form active acids from active esters of acids containing no asymmetric atom (e.g. lactic from pyruvic, etc.); more success has been obtained by Marckwald and McKenzie (1901) and by McKenzie (1904-8), who has accomplished asymmetric syntheses of mandelic, lactic, phenyl-methyl-glycollic and other acids, and of benzoin.

Numerical Relations of Optical Activity.

(*a*) *Homologous Series.*—The work of Tschugaew (1898), Guye (1895), and others shows that, on ascending the normal series of aliphatic acids or amines, the molecular rotation of optically active salts or esters attains an approximately constant value after the first few members of the series have been passed.

(*b*) *Ring-formation.*—It has long been known that anhydrides or lactones derived from active acids show a great difference in rotation from the parent substances, and that substances such as boro-tartrates (1890), probably possessing a structure such as



show greatly enhanced activity.

Haller and Desfontaines (1905) have found the same on formation of active methyl-cyclopentanone derivatives from those of active β-methyladipic esters.

(*c*) *Structural and Position-isomerism.*—The influence of constitution is too great to permit of any definite rules being

formed with reference to ordinary structure isomers, but the effect of *ortho-*, *meta-* and *para*-substitution clearly depends on the nature of the substituent and the proximity to the unsaturated group (Tschugaew, 1898; Cohen, 1905).

(*d*) *Unsaturation* exerts an increasing effect on optical activity (Walden, 1896; Klages and Sautter, 1904), the effect being very much more marked when two unsaturated groups (a "conjugated" system) occur together (Haller, 1899; Hilditch, 1909).

(*e*) *Activity of Electrolytes.*—Landolt (1873) and Oudemans (1879) found that aqueous solutions of mineral salts of active acids or bases possess, when sufficiently dilute, the same molecular rotation, a result which, as Hädrich (1893) pointed out, follows from the ionic theory, the constant value being the rotation of the optically-active ion concerned.

(*f*) The phenomenon of *Muta-rotation* has been known for many years as regards the sugars; it has already been referred to (§ 7).

(*g*) The *Influence of Solvents* on optical activity has been very thoroughly examined by Patterson (1900 and onwards).

Other Elements Obtained in the Optically-active State.—Unsuccessful attempts have been made to resolve asymmetric derivatives of quinquevalent phosphorus (Michaelis, 1901) and arsenic (Michaelis, 1902), and of tervalent iodine (Kipping and Peters, 1900). The following elements have been obtained in optically-active forms:—

(*a*) *Nitrogen.*—Le Bel (1891) partially resolved *r*-methylethylpropylisobutyl-ammonium chloride biochemically; Pope and Peachey (1899) succeeded with *r*-*a*-phenylbenzylallylmethylammonium iodide.[1]

[1] The quinquevalent nitrogen atom has been conceived as acting (i) at the centre of a cube, with valencies directed to 5 of the angles (van 't Hoff, 1878); (ii) at the centre of two superposed tetrahedra (Willgerodt, 1890); (iii) at the centre of a tetragonal pyramid (Bischoff, 1890), which, according to H. O. Jones (1905), best accounts for the changed properties

(*b*) *Tin.*—Methyl-ethyl-propyl stannonium salts were resolved by Pope and Peachey (1900).

(*c*) *Sulphur.*—Smiles (1900) resolved **N**-methylethylphenacyl sulphonium bromocamphorsulphonates and almost simultaneously Pope and Peachey split N-methylethylthetine bromocamphorsulphonate into its active components.

(*d*) *Selenium* compounds were resolved by Pope and Neville (1902) similarly to the second production of asymmetric sulphur mentioned above.

(*e*) *Silicon* compounds, such as ethylpropylbenzyl silicol and sulphonic acids derived from the corresponding silicol oxide have been resolved by Kipping (1904-8) in the course of extensive work on the organic derivatives of silicon.

on alteration of tervalent to quinquevalent nitrogen; and (iv) at the centre of a regular tetrahedron, like carbon, the fifth valency being mobile and of no definite position.

CHAPTER VII

COMPOUNDS AND REACTIONS IN ORGANIC CHEMISTRY

As we remarked in a previous chapter, historical interest attaches rather to general reactions and development of classification than to particular substances, and so in dealing with the organic side of the science, we shall try to indicate the lines along which synthetic methods have developed, the chief classes of reactions which have been discovered, and the chief types of compounds formed thereby.

§ 1. **Hydrocarbons**—The majority of the hydrocarbons have been prepared subsequently to their more important derivatives, but the following list will show how the more notable members of the series came to be found :—

CH_4	*Methane*	Known to van Helmont. First synthesis (CS_2 + H_2S over Cu) by Berthelot, 1858.
C_2H_6	*Ethane*	1848 Frankland (K on C_2H_5CN, and Zn $(C_2H_5)_2$ + H_2O) and Kolbe (electrolysis of potassium acetate).
C_2H_4	*Ethylene*	1795 The "four Dutch chemists". 1866 Tollens (Na on $C_2H_4Cl_2$). 1868 Butlerow (Cu on CH_2I_2 at 100°).
C_2H_2	*Acetylene*	1836 Discovered by Edmund Davy. Synthesized by Berthelot, 1863 (electric arc in hydrogen).
C_6H_6	*Benzene*	1825 Faraday (in coal gas); 1834 Mitscherlich (distilling benzoic acid and lime); 1845 Hofmann (in coal-tar); 1870 Berthelot (synthesis from acetylene).
C_9H_{12}	*Mesitylene*	1868 Fittig; 1838 Kane.
$C_{12}H_{10}$	*Diphenyl*	1866 Berthelot.
$C_{19}H_{16}$	*Triphenylmethane*	1872 Kekulé (benzal chloride + mercury diphenyl).

Other instances have already been given in Chapter vi. (cycloparaffins and hydrocarbons containing conjugated aromatic nuclei).

A number of general methods of *synthesis* for hydrocarbons have been devised from time to time. Such are :—

Electrolysis of alkaline salts of saturated fatty mono- and di-basic and of maleïc or fumaric acids (Kolbe, 1848 ; Kekulé, 1864).

The action of sodium on alkyl halides (Wurtz, 1855).

The action of sodium on a mixture of an alkyl and an aryl halide (Fittig, 1863).

The action of $AlCl_3$ on an aromatic hydrocarbon and an alkyl halide (Friedel and Crafts, 1870).

The action of alcohol on diazo-bodies (Griess, 1866).

Polymerization (acetone to mesitylene, Kane, 1838 ; diacetyl to p-xyloquinone, v. Pechmann, 1889, etc.).

The extensions of the Friedel-Crafts reaction should be noted :—

Preparation of silicon derivatives (Ladenburg, 1875).

Preparation of aldehydes and ketones from acid chlorides and benzenes (Gattermann, 1897).

Preparation of sulphinic acids from sulphur dioxide and benzenes (Knoevenagel, 1908 ; Smiles, 1908).

Preparation of sulphonium bases, etc., from sulphur dioxide and phenolic ethers (Smiles, and Le Rossignol, 1908).

The preparation of hydrocarbons by *reduction* has been effected in numerous instances, of which Berthelot's (fuming hydriodic acid), Baeyer's (reduction of hydroxyl groups by zinc or by phosphorus and hydriodic acid), and the recent method of passing a mixture of hydrogen and the vapour to be reduced over heated finely-divided nickel (Sabatier and Senderens) are the most interesting.

The following methods for the synthesis of polymethylene derivatives may also be cited here :—

The action of sodium on dibromoparaffins (Freund, 1882).

The action of iodine or alkylene dibromides on disodium derivatives of malonic esters (W. H. Perkin, jun., 1894).

Elimination of nitrogen from aliphatic diazo-compounds (Buchner).

Distillation of calcium salts of the fatty dibasic acids (J. Wislicenus, 1893).

Beilstein (1880) noted that Russian petroleum consisted largely of hexamethylenes (naphthenes). Crossley has contributed to the recent knowledge gained on the subject of polymethylene and hydroaromatic derivatives.

Finally, we must refer to the recent work of Gomberg (1900), Tschitschibabin, and others on "triphenylmethyl"; this was at first thought to contain tervalent carbon; other explanations of its formation and reactions, based on the usual assumptions of the valency of carbon, have since been put forward.

§ 2. **Oxygen Derivatives**: (*a*) **Hydroxylic Compounds**—The chief synthetic methods for the most important class of hydroxyl derivatives, the alcohols, have been :—

(*a*) The replacement of halogen, etc., by alkaline hydroxyl.

(*b*) The reduction of aldehydes (Wurtz, 1866) and ketones (Friedel, 1862).

(*c*) The extended action of zinc alkyls on acid chlorides (Butlerow, 1864).

(*d*) The action of magnesium alkylhalides on carbonyl oxygen (Grignard, 1900).

On p. 120 we summarize the history of the more noteworthy alcohols and phenols.

Another section of oxygen derivatives closely allied to the true hydroxylic compounds is that of the *ethers*. The substance which we now call diethyl ether was known as ether, or sulphur ether, to the alchemists, and its preparation from alcohol and sulphuric acid is referred to by the later alchemists and the phlogistic chemists. The name ether was applied on account of the volatile properties of the liquid, and other liquids subsequently discovered, and possessing a similar odour to ether, were also indiscriminately termed ethers. We have already seen (chap. vi.) that much of the discussion on organic theory in the earlier years of the modern era centred round alcohol and ether,

Monohydric Aliphatic Alcohols.		*Discovered.*	*Constitution.*	*Synthesis.*
Primary	CH_3OH Methyl	1661 Boyle	1831 Dumas and Péligot	1858 Berthelot.
	C_2H_5OH Ethyl	(Known to early alchemists as "*aqua vitae*". Basil Valentine noted its combustibility, Lully its solvent powers, and Libavius gave it its modern name—*alcohol*—a word formerly used in other senses.)		
	$C_5H_{11}OH$ Amyl	1837 Cahours.		
	$C_{16}H_{33}OH$ Cetyl	1818 Chevreul ("æthal," from spermaceti).		
Secondary	C_3H_7OH Isopropyl	1855 Berthelot (from propylene).		
		1862 Friedel (from acetone).		
Tertiary	$(CH_3)_3C.OH$ Butyl	1863 Butlerow (zinc methyl and acetyl chloride).		
Unsaturated	$C_3H_5.OH$ Allyl	1856 Cahours and Hofmann.		
Aromatic	C_7H_7OH Benzyl	1853 Cannizzaro (KOH and benzaldehyde).		
	$C_7H_6(OH)_2$ Saligenin	1845 Piria (from salicin).		
Dihydric	$C_2H_4(OH)_2$ Glycol	1854 Williamson and Kay (cf. chap. vi. p. 85).		
	$R.CH(OH)$ | $R.CH(OH)$ Pinacones	1858 Fittig (alkaline reduction of ketones and aldehydes).		
Trihydric	$C_3H_5(OH)_3$ Glycerol	1779 Scheele.	1853 Berthelot.	1872 Friedel and Silva.
Tetrahydric	$C_4H_6(OH)_4$ Erythrol	1848 Stenhouse.	1893 Grier (synthetically).	
Hexahydric	$C_6H_5(OH)_6$ Mannitol	1806 Proust.		
Phenols	C_6H_5OH Phenol	1834 Runge (in coal-tar).	First used as disinfectant, 1867 (Lister).	
	$C_6H_4(OH)_2$ Pyrocatechol	1839 Reinsch (distillation of catechin).		
	,, Hydroquinone	1848 Wöhler (from quinine acid).		
	$C_6H_3(OH)_3$ Pyrogallol	1786 Scheele (from gallic acid).		
	,, Phloroglucinol	1855 Hlasiwitz (from phloretin).		
	$C_6(OK)_6$ Potassium hexaoxybenzene	1834 Liebig; more thoroughly 1886, Nietzski and Benckiser.		
	$C_{10}H_7(OH)$ α-Naphthol	1863 Schulze (in coal-tar).		
	,, β- ,,	1863 ,, ,,		
	$C_6H_2(NO_2)_3(OH)$ Picric acid	1799 Welter (nitration of silk); 1842 Laurent recognized it as a phenol.		

and in consequence of this the distinction between "simple" ethers and "compound" ethers (later called *esters*) was soon observed. We may recall at this point how Williamson (and, independently, Chancel) finally solved the problems of the constitution of ether and of its production by the sulphuric acid process, showing at the same time how "mixed" "simple" ethers of the type R—O—R^1 could exist. The anæsthetic properties of ether were discovered by Jackson (1842). Mention may also be made of the class of phenolic ethers, of which anisol, $C_6H_4OCH_3$ (discovered by Cahours, 1841), may be taken as typical. The discovery of some characteristic esters is recalled in the following table:—

Ethyl acetate	1759 Lauroguais.
,, chlorcarbonate	1833 Dumas (phosgene and alcohol).
Ethylene dichloride	1795 Four Dutch chemists (ethylene + Cl_2).
,, dibromide	1826 Balard (ethylene + Br_2).
,, di-iodide	1821 Faraday (sunlight on ethylene + I_2).
Chloroform	1831 Liebig; Soubeiran, 1847, used in surgery (Simpson).
Iodoform	1832 Serullas.
Ethyl hydrogen sulphate and ethionic acids	1833-40 Hennel, Serullas, Magnus and Regnault.
Ethyl hydrogen phosphate	1833 Pélouze.
,, ,, carbonate	1840 Mitscherlich.
Glyceryl trinitrate	1847 Sobrero ("nitro-glycerine").

(The products of the action of HNO_3 on ethyl alcohol were studied by Debus, 1856.)

§ 3. **Oxygen Derivatives**: (*b*) **Carbonyl Compounds, Reactions of Condensation**—Aldehydes and ketones have been prepared chiefly by the oxidation of alcohols (Scheele, 1774), the distillation of calcium salts of fatty acids (Williamson), the action of zinc alkyls on acid chlorides (Freund, 1860), Gattermann's aluminium chloride reaction (cf. p. 118) and Grignard's reaction (1900; the action of magnesium alkyl halides on form-alkylanilides, formic ester, and iso-nitriles (aldehydes) and on nitriles and amides (ketones)). The

detection of the carbonyl group has been effected by hydroxylamine (oximes, V. Meyer, 1882) and phenylhydrazine (E. Fischer, 1877). The development of a series of "condensation reactions" of aldehydes and ketones (reactions accompanied by elimination of the elements of water or alcohol) may here be dealt with :—

(*a*) The *aldol condensation* of aldehydes or ketones in presence of acid or alkali, e.g. $CH_3CHO + CH_3.CHO \rightarrow CH_3.CH(OH).CH_2.CHO$ (*aldol*) $\rightarrow CH_3.CH:CH.CHO$ (crotonaldehyde). Wurtz (1872) studied this particular case, but in 1866 Baeyer had observed the similar formation of mesityl oxide and phorone from acetone.

(*b*) The *benzoin condensation* first noticed by Liebig and Wöhler (1832) in the action of KCN on benzaldehyde, but only satisfactorily explained by Lapworth in 1903.

(*c*) The *Claisen condensation* of carbonyl derivatives with substances containing the keten group $—CH_2—CO—$; examples of compounds so formed are benzalacetone (Claisen, 1881); o-nitrobenzalacetone (Baeyer, 1882; used in indigo-synthesis), cinnamalacetone (Einhorn and Diehl, 1885), α-acrose (dl-fructose) (E. Fischer, 1887, from formaldehyde), and ionone (Tiemann, 1893, from citral).

The historically noteworthy members of this group appear on the opposite page.

§ 4. **Oxygen Derivatives:** (*c*) **Carboxylic Acids**—The importance of this class for the determination of constitution and other problems is obviously very great, and consequently a very large number of syntheses have been devised; we have only space to refer to a few, such as oxidation of alcohols or aldehydes, saponification of nitriles [Dumas and Frankland and Kolbe (1847), acetoacetic and malonic ester syntheses (cf. § 5), and metal-alkyl syntheses ($Na + CO_2 + C_6H_5Br$, Kekulé, 1866; finely-divided silver on halogen fatty acids, J. Wislicenus, 1868; zinc on chloracetic and oxalic esters, Fittig and Daimler, 1887; zinc on ketones and iodacetic esters, Reformatski, 1887, used in synthesis of citric acid, Lawrence, 1897); Grignard reaction]. Perkins' reaction for the preparation of *ethylenic acids* by heating a mixture of aldehyde, sodium fatty acid salt and acid

Aldehydes Aliphatic	H . CHO Formaldehyde	1868 Hofmann.
	CH_3 . CHO Acetaldehyde	1774 Scheele (alcohol oxidation); 1821 Döbereiner (isolated aldehyde ammonia); 1835 Liebig (composition and name); Polymers: metaldehyde (Liebig, 1835), and paraldehyde (Fehling, 1838).
	CCl_3 . CHO Chloral	1832 Liebig.
	C_3H_5 . CHO Crotonaldehyde	1872 Kekulé.

(Cf. also the sugars, chapter viii.)

Ketones	$(CH_3)_2CO$ Acetone	Known to alchemists as the "quintessence". Composition by Liebig.
Diketones	$C_2H_2O_2$ Glyoxal	1856 Debus (alcohol and nitric acid).
	α-Diketones	1887 v. Pechmann (from isonitrosoketones).
	β- ,,	1889 Claisen (condensation of ketones and acetic esters).
		1888 Combes and Gustavson (aluminium chloride on acetyl chloride).
Aromatic	C_6H_5 . CHO Benzaldehyde	1831 Liebig and Wöhler (from amygdalin).
	$C_6H_4(OH)$. CHO Salicylaldehyde	1839 Piria (oxidation of salicin).
	$C_6H_3(OCH)(OH)CHO$. Vanillin	1874 Tiemann and Haarmann (artificial preparation).
Quinones	$C_6H_4O_2$ Quinone	1838 Woskresenski (from quinic acid). Named by Berzelius.
	$C_{10}H_6O_2$ α-Naphthaquinone	1869 Hermann.
	$C_{14}H_8O_2$ Anthraquinone	1835 Laurent; 1861 Anderson.
	$C_8H_8O_2$ p-Xyloquinone	1889 v. Pechmann (condensation of diacetyl).

anhydride (1868, coumaric; 1875, cinnamic acid) has been studied in addition by Baeyer, Conrad, Fittig, and others, but its precise mechanism is not quite definitely understood. In the course of his work Fittig was able to shed much light on the constitution of lactones (paraconic acids, 1894-1904), and to confirm the ideas put forward by Erlenmeyer, sen. (1880), to account for Saytzew's butyrolactone (1873) and Bredt's isocaprolactone (1880).

The structure of *amido-acids* (see also chap. viii.) was defined when Perkin and Duppa obtained glycocoll (already prepared from glue (Braconnot, 1820), hippuric acid (Dessaignes, 1846), and bile (Strecker, 1848)) by the action of ammonia on bromoacetic acid in 1858, and that of *oxy-acids* followed, since glycocoll had been submitted to the action of nitrous acid (Strecker, 1848). The latter have also been prepared by the action of zinc alkyl halides on oxalic ester (Frankland and Duppa, 1865), from aldehyde cyanhydrins (Wislicenus, 1862) and from Grignard's reagent and ketonic esters (McKenzie, 1905).

The first *nitriles* to be prepared seem to have been proprionitrile (1834, Pélouze, $Ba(C_2H_5)SO_4 + KCN$), aceto-nitrile (1847, Dumas, phosphoric anhydride and ammonium acetate) and benzonitrile (1844, Fehling). With the anhydrides (Gerhardt, 1852) may be mentioned the *acid peroxides* (Brodie, 1864, from the former and BaO_2). Various improvements have been made in the preparation of *acid chlorides* since Liebig and Wöhler produced the first member in 1832 by the chlorination of benzaldehyde, such as the interaction of the sodium salts with phosphorus pentachloride (Cahours, 1846), trichloride (Béchamp, 1856), oxychloride (Gerhardt, 1851), or thionyl chloride (Hermann, 1883). Reference must finally be made to the *amides*, such as oxamide (from ammonium oxalate, Dumas, 1830; ammonia and oxalic ester, Liebig, 1834), benzamide (ammonia and benzoyl chloride, Liebig and Wöhler, 1832), acetamide (Dumas, 1847) and the *anilides* (Gerhardt, 1845).

Details of interest are connected with the following acids :—

Aliphatic	$H.COOH$ Formic	1700 Wray.
Monobasic	$CH_3.COOH$ Acetic	Known to the ancients; concentrated by distillation, Geber; glacial, during phlogistic period; composition, Berzelius (1814); relation to alcohol, Döbereiner, 1821; synthesis, Kolbe and Melsens (1842).
Dibasic	$(COOH)_2$ Oxalic	1776 Scheele; 1829 Gay-Lussac (KOH on wood); 1868 Drechsel ($Na + CO_2$).
	$CH_2(COOH)_2$ Malonic	1858 Dessaignes (from malic acid); 1864 Kolbe (synthetically).
	$C_2H_4(COOH)_2$ Succinic	1550 Agricola (distillation of amber); 1861 Simpson ,,
	$C_4H_8(COOH)_2$ Adipic	1837 Laurent (from fats by oxidation).
Oxyacids	$CH_2(OH)COOH$ Glycollic	1848 Strecker (from glycocoll); 1856 Debus (oxidation of alcohol).
	$C_2H_3(OH)COOH$ Lactic	1780 Scheele (in sour milk); 1808 Berzelius (sarcolactic acid in muscles).
		1847 Liebig showed the difference in the two acids.
		1873 J. Wislicenus ,, ,, to be due to stereo-isomerism.
	$C_2H_3(OH)(COOH)_2$ Malic Salts known to iatro-chemists.	Acid, 1785, Scheele; 1832 Liebig (composition).
	$C_2H_2(OH)_2(COOH)_2$ Tartaric Salts	,, ,, Acids (dextro), 1769 Scheele; (racemic) 1822. Kestner. Synthesis of racemic and meso-acids, 1861, Kekulé, Perkin and Duppa.
Unsaturated	$C_2H_2(COOH)_2$ Fumaric	1845 Pfaff. Constitution Le Bel-Van 't Hoff, 1874. Oxidized to *r*-tartaric, 1880 Kekulé-Anschütz.
	,, Maleic	1844 Lassaigne. Constitution Le Bel-Van 't Hoff, 1874. Oxidized to meso-tartaric, 1880 Kekulé-Anschütz.
Aromatic	C_6H_5COOH Benzoic. From gum-benzoin by iatro-chemists	1832 Liebig and Wöhler (composition).
	$C_6H_4(NH_2)COOH$ Anthranilic	1841 Fritzsche (indigo and caustic potash).
	$C_6H_4(OH)COOH$ Salicylic	1838 Piria (from salicylaldehyde); 1843 Cahours (connexion with oil of wintergreen); 1860 Kolbe (manufacture from phenol).
	$C_6H_4(OCH_3)COOH$ Anisic	1839 Cahours (in anise oil); 1863 Saytzew (conversion to *p*-oxybenzoic acid).
	$C_6H_4(COOH)_2$ Phthalic	1836 Laurent (from naphthalene).
	$C_6(COOH)_6$ Mellitic	1799 Klaproth (from the mineral "honeystone" (the aluminium salt)).
		1870 Baeyer explained its constitution.
	C_6H_7COOH Cinnamic	1834 Dumas and Péligot; 1856 Bertagnini (benzaldehyde and acetylchloride).
		1875 Perkin's synthesis; 1890 Claisen (condensation of acetic ester and benzaldehyde).
Non-	HCN Prussic	1782 Scheele ($H_2SO_4 + K_4Fe(CN)_6$); 1811 Gay-Lussac (anhydrous).

§ 5. **Oxygen Derivatives:** (*d*) **Ketonic Acids**—This section of the organic acids is particularly important, because many of its members (all those possessing the group —CH_2 – CO—) are able, by virtue of the acidic properties of the methylene hydrogen atoms, to enter into all manner of complex synthetic reactions. The following are typical :—

(*a*) Action of chlorcarbonic esters on the sodium compounds of acetoacetic ester, malonic ester, etc. (1877 Conrad; 1882-6 Bischoff; in 1879 Conrad undertook a comprehensive investigation of the malonic ester syntheses, foreshadowed by van 't Hoff in 1874).

(*b*) Action of iodine on the sodium compounds (dioxysuccinic esters, Bischoff, 1884).

(*c*) Action of alkylene bromides on the sodium compounds (Bischoff, 1880-8; Perkin, jun., 1902).

(*d*) Condensation of phenanthraquinone and acetoacetic ester by ammonia (Japp and Streatfield, 1883).

(*e*) Condensation of aldehydes and acetoacetic ester by organic bases (Knoevenagel's reaction, 1893).

(*f*) Condensation of olefinic or acetylenic esters with sodium compounds of acetoacetic, malonic, or cyanoacetic esters (Michael's reaction, 1887).

(*g*) Condensation of hydrazines, etc., and ketonic esters, yielding heterocyclic bodies (cf. § 8).

The parent member of the *polyketides*, as Collie (1907) has proposed to term substances containing the —CH_2 . CO— group, is *keten* $CH_2 : CO$, isolated by Wilsmore and Stewart (1907); substituted ketens have been prepared by Staudinger from bromacyl bromides and zinc, while a new oxide of carbon, carbon suboxide C_3O_2, prepared by distilling malonic ester and phosphoric anhydride (1906, Diels and Wolf), appears to be a keten derivative, $CO : C : CO$. *Acetylketen* is a polymer of keten, and an internal anhydride of acetoacetic acid (Chick and Wilsmore, 1908).

Typical ketonic acids are :—

$CH_2 . CO . COOH$ Pyruvic; obtained by iatro-chemists in distilling "tartar," and by Berzelius (1835).

$CH_3CO . CH_2 . COOH$ Acetoacetic (referred to in chap. vi.).

$CH_3CO . CH_2 . CH_2 . COOH$ Laevulinic; 1874 v. Grote and Tollens.

$CO(CH_2 . COOH)_2$ Acetonedicarboxylic; 1884 v. Pechmann (from citric acid).

$C_6H_5 . CO . CH_2 . COOH$ Benzoylacetic: 1884 Perkin (phenyl-propiolic and strong sulphuric acid); 1887 Claisen (condensation of benzoic and acetic esters).

§ 6. **Nitrogen Derivatives**—These have been very fully studied during the past century, since the constitution of so many vegetable and animal products, as well as the preparation of dyes, explosives and other technically valuable substances depends on the function of the nitrogen-containing group.

Commencing with *nitro-compounds* (the first of which, excluding picric acid, was nitrobenzene, Mitscherlich, 1834), we notice the evolution of methods of nitration in the aromatic series, and the preparation of the first aliphatic members by Kolbe and by V. Meyer in 1872. The latter extended his studies to the conversion of nitro-paraffins to nitrols, nitrolic acids, etc. *Nitroso* compounds were obtained by the action of mercury diphenyl and nitrosyl bromide (Baeyer, 1874), and of nitrous acid on secondary amines and on phenols (Baeyer and H. Caro, 1874, 1874).

The *amido*-derivatives form the most important class of nitrogen compounds. Aliphatic amines have been prepared by intraction of alkyl isocyanates and caustic potash (Wurtz, 1848), alkylation of ammonia (Hofmann, 1849), reduction of nitriles (Mendius, 1862), and hydrolysis of isonitriles (Hofmann, 1868); Hofmann (1885) also illustrated the conversion of amides (by bromine and potash) to the next lower amine. Besides Hofmann's alkylation of aniline, aromatic amines have been prepared by reduction of nitro-compounds by ammonium sulphide (Zinin, 1841), hydrochloric acid and zinc (Hofmann, 1845), iron (Béchamp, 1852) or tin (Roussin), and electrolytically (Löb, 1900). The electrolytic reduction of nitrobenzene, in particular, has led under suitable conditions to methods for the preparation of azoxy-, azo-, hydrazo-, or amino-benzene. The following individual amines and related derivatives are worthy of note:—

Aniline (1826 Unverdorben, distillation of indigo; 1834 Runge, "cyanol" in coal-tar; 1841 Fritzsche, "aniline," from indigo and potash; 1841 Zinin, reduction of nitrobenzene—all four substances proved identical by Hofmann, 1843); p-toluidine (1845, Hofmann); diphenylamine (1864, Hofmann, from rosaniline); azoxybenzene (Mitscherlich, 1834); hydrazobenzene (Hofmann, 1863), which changes so readily to the isomeric benzidine (already obtained by Zinin in 1845 by acid reduction of azo-benzene, the intermediate hydrazo-compound being overlooked); and α- and β-naphthylamines (Zinin, 1842; Liebermann, 1876). The constitution of the numerous intermediate reduction products of nitrobenzene is mainly due to Erlenmeyer and Kekulé.

The derivatives of *hydrazine* belong here and include phenylhydrazine (E. Fischer, 1875, who obtained it from potassium phenylhydrazine sulphonate, previously prepared by Strecker in 1871), and the alkylhydrazines (E. Fischer, 1879).

Other amino-compounds are :—

$CO(NH_2)_2$ Carbamide	1773 Rouelle (in urine); 1828 Wöhler (from ammonium cyanate).
$C(NH)(NH_2)_2$ Guanidine	1861 Strecker (oxidation of guanine).
$CN \cdot NH_2$ Cyanamide	1838 Bineau ($CNCl + NH_3$); recently introduced as a manure.

The first *diazo-compounds* were obtained by Griess in 1863 from aniline; the problem of their constitution has already been discussed (ch. vi. § 7). The discovery of diazo-amidobenzene and its conversion to amido-azobenzene (Griess, 1862) was of great importance to the dyeing industry. Other interesting diazo-bodies are :—

$C_6H_5.N<\begin{matrix}N\\ \|\|\\ N\end{matrix}$ Diazoimidobenzene	1866 Griess.
$CH_2<\begin{matrix}N\\ \|\|\\ N\end{matrix}$ Diazomethane	1894 V. Pechmann (alkalies and nitrosoamines).
$CO_2C_2H_5 \cdot CHN_2$ Diazoacetic ester	1883 Curtius (nitrous acid and glycocoll).
$CH_3 \cdot N{=}N \cdot NH \cdot R$ Aliphatic diazo-amido compounds	1907 Dimroth (Grignard reagent and diazo-paraffins).

There remain, in conclusion, the *isonitriles* (predicted by Kolbe, and discovered at about the same time by Gautier

(alkyl iodides and silver nitrate) and Hofmann (chloroform, primary amine, and alkali) in 1866), and the *isonitroso* compounds, including the oximes (Victor Meyer, 1883 and the compounds formed by the action of nitrous acid (or amyl nitrite) on the methylene group —CH_2— under suitable conditions (V. Meyer, 1882).

Other nitrogenous compounds will be mentioned in connexion with the history of alkaloids, proteins, dyestuffs, etc.

§ 7. **Derivatives of Elements other than Oxygen or Nitrogen**—The researches in this direction group themselves into three main classes :—

(*a*) The study of compounds analogous to the amines.

(*b*) The study of sulphur compounds.

(*c*) The study of "organo-metallic" derivatives.

(*a*) To this section belongs the work on the alkyl derivatives of phosphorus, arsenic, and antimony. Aliphatic tertiary phosphines were discovered by Thénard in 1846 (from alkyl iodides and calcium phosphide), while Hofmann prepared the primary and secondary bases by his alkylation method in 1871. Aromatic phosphines ($C_6H_5PH_2$, $C_6H_5PO_2$ and $C_6H_5P : PC_6H_5$) were derived by Michael in 1876 from $C_6H_5PCl_2$. Tertiary and quaternary arsenic and antimony compounds have been chiefly studied by Löwig and Landolt (1853); the primary and secondary arsenic derivatives were found to be non-basic, the primary (mono-methyl) bodies being due to Baeyer (1858). The secondary compounds are of especial interest, for they form one of the three "pillars" of the older radical theory, and were studied much earlier than any of the others. They were investigated by Bunsen (1837-43), who isolated many derivatives of "cacodyl" $(CH_3)_2As$— from "Cadet's fuming arsenical liquid," first prepared in 1760 by Cadet by distilling arsenious acid and potassium acetate.

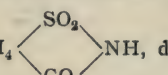
(*b*) Organic sulphur compounds have been found to contain bi-, quadri-, or sexa-valent sulphur, and while the bi- and sexa-valent compounds are now well defined there is still room for improvement in our knowledge of the behaviour of many substances containing quadrivalent sulphur.

The bi-valent derivatives include the mercaptans and sulphides (C_2H_5SH, discovered by Zeise, 1834; $(C_3H_5)_2S$, allyl sulphide, isolated from garlic by Wertheim, 1844; C_6H_5SH, Kekulé, 1867); derivatives of thiocarbonic acid (CS_2, Lampadius, 1796, from pyrites and coal; COS, v. Than, 1867; xanthates RO.CS.SK, Zeise, 1824, from CS_2, alcohol and soda); $CS(NH_2)_2$ thiourea, Reynolds (1869, from NH_4CNS); thioacetic acid

$CH_3 . COSH$, Kekulé, 1854; and the mustard oils (alkyl isothiocyanates, $R . N : C : S$) of which allyl isothiocyanate (in mustard seeds) was the first to be isolated (Bussy, 1840), and whose constitution and synthesis were worked out by Hofmann about 1868.

The most interesting quadrivalent sulphur compounds are the sulphinic acids (aliphatic, 1857, Hobson; aromatic, 1862, Kalle), sulphoxides (1866, Saytzew) and sulphonium bases (aliphatic, 1865, Cahours; aromatic, Smiles and Le Rossignol, 1906). Thionyl derivatives of amines, $R . N : SO$, have been studied by Michael (1891). It is probable that the constitution of not a few dyestuffs containing sulphur will be shown to depend upon the presence of quadrivalent sulphur.

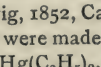
The sexavalent derivatives are perhaps the best known, such as the sulphonic acids (methylsulphonic, Kolbe, 1845, benzene sulphonic, Mitscherlich, 1833; sulphanilic (p-aminobenzenesulphonic), Gerhardt, 1845 (sulphonation of aniline); and the many dyes which are used in the form of sulphonic acids for the sake of superior solubility), and the sulphones (Saytzew, 1867; α-disulphones $R . SO_2 . SO_2R$, Kohler and Macdonald, 1899, and Hilditch, 1908; sulphonal $(CH_3)_2C(SO_2C_2H_5)_2$ discovered by Baumann (1888), and applied as a soporific by Kast (1889); saccharin



$C_6H_4 \begin{matrix} SO_2 \\ CO \end{matrix} NH$, discovered by Remsen and Fahlberg (1879) in the alkaline oxidation of *o*-toluene sulphonamide).

(*c*) The organic compounds of *silicon* have proved interesting since Wöhler in 1863 showed their close analogy to the corresponding carbon derivatives, and the chief workers have been, for the aliphatic compounds, Frankland (zinc alkyls and $SiCl_4$) and Friedel and Crafts (1863); for aromatic derivatives, Ladenburg ($C_6H_5SiCl_3$, 1874) and Polis ($(C_6H_5)_4Si$, 1886). Kipping has recently prepared many new silicon derivatives by the action of different magnesium alkyl iodides on silicon tetrachloride (1907).

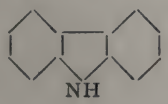
Alkyl compounds of other metals followed chiefly upon Frankland's discovery of zinc ethyl in 1849, and were prepared from the zinc alkyls and metal chlorides, e.g. tin (Löwig, 1852, Cahours, 1860); lead ($Pb(C_2H_5)_4$, Buckton, 1859). Mercury alkyls were made from sodium amalgam and the alkyl iodides (Frankland, 1864; $Hg(C_6H_5)_2$, Otto and Dreher, 1870).

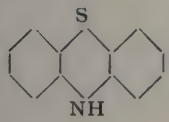
The zinc alkyls are exceedingly difficult to manipulate, and Fleck (1893) found the magnesium compounds even worse; Barbier, however, found that a mixture of finely-divided magnesium and methyl iodide acted readily and with the same result as the alkyl derivative (1899), and in 1900 Grignard made an extensive study of the reaction between magnesium and alkyl halides, showing how the compounds formed  could be used

in all manner of syntheses (Grignard's reagent). Pfeiffer has applied the reagent to various metallic chlorides and has obtained in this way alkyl derivatives of mercury, thallium, bismuth, platinum and other metals.

§ 8. **Heterocyclic Compounds**—Dozens of ring-systems consisting of carbon, oxygen, sulphur and nitrogen atoms have been synthesized within the last forty years, and historical data of the chief members of these have already been furnished (chap. vi. p. 91); it remains to give some idea at this point of the manner in which the methods of synthesis of the various types have developed, and we may confine our attention to the five- and six-membered rings, the rest being relatively unimportant. The synthetic reactions may be grouped as follows :—

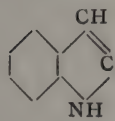
I. *Pyrogenetic reactions* :—

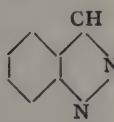
Carbazole  (Gräbe, 1873; from diphenylamine).

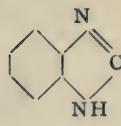
Thiodiphenylamine  (Bernthsen, 1888; diphenylamine and sulphur).

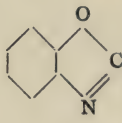
Pyrimidines (E. v. Meyer, 1889; polymerization of nitriles).

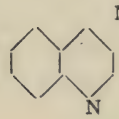
II. *Reduction reactions* :—

Indol  (Baeyer, 1869; from *o*-nitrocinnamic aldehyde).

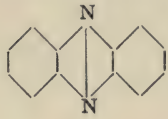
Indazoles  (Nölting, 1890; from *o*-nitro compounds)

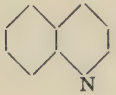
Benzimidazoles  (Hobrecker, 1872; from *o*-nitro compounds).

Benzoxazoles  (Hübner, 1881; from benzoyl-*o*-nitrophenols).

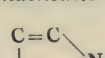
Quinoxalines  (Hinsberg, 1896; from *o*-nitrophenyl-α-amido-acids).

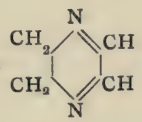
III. *Oxidation reactions* :—

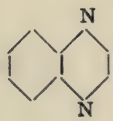
Phenazines  (Ris, 1886; from *o*-diamines and α-naphthol).

Quinolines  (Skraup, 1880; from anilines and glycerol).

IV. *Condensation reactions* (*a*) from *α-diketones* :—

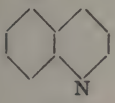
Glyoxalines  (Rodziszewski, 1882; with ammonia and aldehydes).

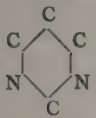
Dihydropyrazines  (Weil, 1900; with alkylene diamines).

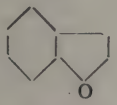
Quinoxaline  (Hinsberg, 1887; with *o*-diamines).

(*b*) from *β-diketones* :—

Pyridines (Hantzsch, 1882; with aldehyde ammonia).

Quinolines  (Knorr, 1886; anilides of β-keto-acids).

Pyrimidines  (Pinner, 1893; with acid amidines).

Coumarones  (Hantzsch, 1886; chloroacetoacetic ester and phenates).

(*c*) from *γ-diketones* :—

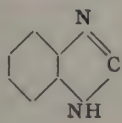
Furfuranes (Paal, 1885; elimination of water).

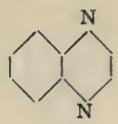
Thiophenes (Paal, 1885; with phosphorus pentasulphide).

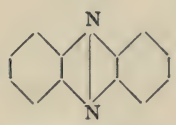
Pyrrols (Paal, 1885; with ammonia).

Thiophenes (Volhard and Erdmann, 1885; sodium succinate and P_2S_5).

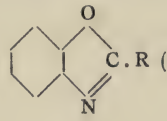
(*d*) from *o-diamines* :—

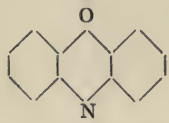
Benzimidazoles  (Ladenburg, 1875; with fatty acids).

Quinoxaline  (Hinsberg, 1887; with cyanogen).

Phenazine  (Hinsberg, 1896; with *o*-quinones or pyro-catechol).

(*e*) from *o-aminophenols*:—

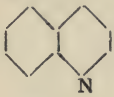
Benzoxazoles  (Ladenburg, 1877; with fatty acids).

Phenoxazine  (Bernthsen, 1887; with pyrocatechol).

(*f*) from *amino-aldehydes or ketones*:—

Oxazoles (Blümlein, 1884; α-chlorketones and amides).

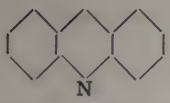
Pyridine (Schiff, 1861; aldehyde-ammonia and aldehydes).

Quinoline  (Friedlander, 1883; *o*-aminobenzaldehydes and —CH_2.CO— compounds).

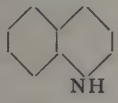
Pyrazine (Skraup, 1893; aminoaldehydes and aminoketones).

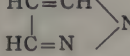
(*g*) from *amino-acids*:—

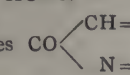
Pyridine (Böttinger, 1881; from glutaconamic acid).

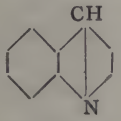
Acridine  (Bernthsen, 1884; from diphenylamine and acids).

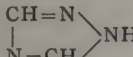
(*h*) from *hydrazine and hydroxylamine* :—

Indol  (E. Fischer, 1886; from certain phenylhydrazones).

Pyrazoles  (Claisen, 1888; hydrazines and β-diketones).

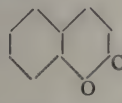
Pyrazolones  (Knorr, 1883; phenylhydrazine and β-ketonic esters).

Indazoles  (Fischer and Tafel, 1885; from *o*-hydrazine cinnamic acids).

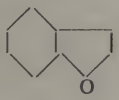
Triazoles  (Andreocci, 1892; acid hydrazides and amides).

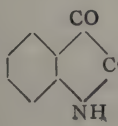
Isoquinoline (Bamberger, 1894; from cinnamaldoxime).

(*i*) *Perkin's reaction* :—

Coumarin (α-Pyrone)  (Perkin, 1865; from salicylaldehyde and acetic anhydride).

(*j*) *Alkaline condensation or decomposition* :—

Coumarone  (Fittig, 1883; from coumarin (loss of CO)).

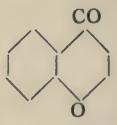
Isatin  (Baeyer, 1880; alkalies on *o*-nitrophenylpropiolic acid).

Other points of interest which may be chosen from the history of the heterocyclic group are:—

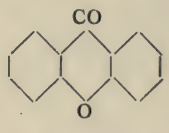
(*a*) The furfurane, thiophene and pyrrol compounds, which present so close an analogy to the benzene and pyridine derivatives in many ways, although this relation and the cognate relationships of coumarone, indol, carbazole, etc., to the three first-named bodies were not generally recognized till about 1885.

(*b*) The connexion found to exist between a large number of natural products, notably certain vegetable dyes (quercetin, fisetin, etc.), and the γ-pyrone compounds

pyrone

, benzopyrone 

and

xanthone 

which have been the subject of study by Kostanecki, A. G. Perkin, and others of recent years.

(*c*) The importance of many derivatives of pyridine, quinoline and isoquinoline (especially the carboxylic acids) for the determination of the constitution of the alkaloids, most of which yield on rupture of their complicated molecules one or more of these simple decomposition-products.

CHAPTER VIII

THE CHEMISTRY OF PLANT AND ANIMAL LIFE

§ 1. **Chemical Processes in the Vegetable and Animal Kingdoms**—Although many of the alchemists professed to regard their science as being, by reason of its connexion with the process of life, too sacred and mysterious for the average person to understand, there came a time when botanists and physiologists were inclined to disparage the utility of any chemical explanation of vital processes, holding that these were caused by a "vital force" of a nature entirely different to the ordinary inorganic "chemical affinity". In spite of all the chemical work, such as Lavoisier's analyses of typical organic bodies and Wöhler's or Kolbe's syntheses of organic from inorganic materials tending to prove that there was nothing chemically anomalous about an organic compound, this opinion held general sway until about the middle of the nineteenth century. Perhaps it is partly in consequence of this that the first modern investigations on the chemical reactions going on in plant or animal life were undertaken in most cases by chemists rather than physiologists. In this way Fourcroy, Vauquelin, and later, Berzelius, studied animal chemistry, while Senebier, Dutrochet and especially Saussure worked out the conditions under which carbonic acid is absorbed and the carbon assimilated by plants, noting that certain parts of plants evolve instead of absorbing the gas and that a small evolution of heat also takes place, thus forming an analogy with animal breathing.

One of the important problems in both plant and animal realms is nutrition, and the chemical nature of the subject be-

came plain through the researches just mentioned and especially by the work of Liebig, who embodied his results in a pamphlet published about 1842. With reference to animal nutrition, he stated that it was based upon a series of chemical reactions and distinguished between real nutrients and substances which effect animal change but do not build up the tissues; he disproved the theory (which at that time had held sway for about a century) that plants are nourished by a certain "humus" in the soil, and showed that in reality they live on water, carbonic acid, ammonia, nitric acid, silica, and in lesser degree elements such as phosphorus, sulphur, magnesium, calcium, iron, potassium, which are built up into complex compounds in the vegetable cells.

This work is of course the foundation of scientific agriculture, which consists in supplying to a crop the correct amount of the constituents needful for its particular development. Very much work has been done since Liebig's time on the composition of soils, and agricultural chemistry is to-day a science in itself, special laboratories being scattered over Europe and some of the British colonies for the investigation of plant-chemistry and the guidance of the farmer.

At the same time the selection of human food has been based upon more scientific ground owing to the work of Liebig Pettenkofer, Voit, and many others, while the importance of controlling its quality is now generally recognized, as evidenced by the numerous official analysts engaged in the work and the recent creation (1908) of an annual international congress to advise upon legislation respecting matters of food and hygiene.

Moreover, the rapid extension of structural knowledge in organic chemistry has encouraged the isolation of many of the complicated substances occurring in living things with a view to elucidating their constitution. Thus chlorophyll, the colouring matter of leaves, has been repeatedly studied (Sachs, Pringsheim, etc.), and has quite recently been obtained in a crystalline state by Willstätter. Similarly blood (with its components hæmo-

globin, hæmatin, etc.) has frequently received attention (Magnus, Meyer, etc. etc.), and so have other organs and products of the animal metabolism such as flesh (Liebig, Strecker, Helmholtz, Brücke), fats and milk (Chevreul), saliva (Leuchs discovered the enzyme *ptyalin*, 1831; Ludwig, Brücke), gastric juice (Kühne), and urine (Liebig and Voit estimated urea; Wöhler and Dessaignes showed formation of hippuric acid; etc.), the names simply indicating one or two of the foremost workers.

Side by side with the efforts to ascertain the structure of vegetable and animal products such as the alkaloids, or sugars, numerous attempts have been made to produce them by synthesis, and in not a few cases these have been attended with success. Nevertheless it has often been remarked that such syntheses resemble the natural process in little more than the identity of the end-product, for plants and animals only have recourse to agents such as phosphorus pentoxide or pentachloride, potassium cyanide, caustic soda, or strong sulphuric acid (to name a few of the favourite synthetic laboratory reagents) under the most abnormal and dismal conditions.

We cannot unfortunately trace the interesting story of biological chemistry in further detail, but must confine ourselves to a description of the chemical development of four important classes of naturally occurring organic products, viz. the alkaloids, the terpenes, the sugars and other "carbohydrates," and the purines, proteins and allied nitrogenous substances.

§ 2. **The Alkaloids**—The presence of crystalline basic substances in certain plant-juices was not recognized until rather more than a century ago, when Séguin prepared "morphium" from opium (1803). "Morphium" was soon found to be a mixture of several bases, from which one, morphine, was isolated in the pure state by Sertuerner in 1817. Other allied bodies such as strychnine, quinine, coniine were rapidly discovered and the generic name of alkaloids was given to them on account of their basic properties. Later on, Liebig showed that the latter was due to the nitrogen present in all the compounds concerned,

and much more recently, when the constitutions of the fundamental types of organic compounds had been worked out, it was found that most alkaloids could be broken down by more or less violent means into simpler bodies, allied to pyridine (Königs, Ladenburg, Weidel). In consequence of this and of the preparation of artificial complex pyridine bases, the term alkaloid is now generally considered to embrace all basic complex derivatives of pyridine or other heterocyclic nitrogenous ring-system.

Most of the alkaloids have marked therapeutic (toxic or anæsthetic) properties and considerable attention has therefore been paid to their detection by a variety of reagents, such as double metal halides (Pettenkofer, 1844), phosphomolybdic acid (Sonnenschein, 1856), polyiodides (Jörgensen, 1870), or hydroferrocyanic acid (E. Fischer, 1877).

So various have been the methods for determining alkaloid structure and attempting alkaloid synthesis that it is impossible to name them here; we can only give a summary (p. 141) of the chief men connected with the more important alkaloids (with the approximate date of their work) and mention that the most prominent workers in this have been Pelletier and Caventou (1829), Liebig (1835), Regnault (1840), Laurent (1845), Anderson (1850), Ladenburg (1870-), Skraup (1880), Freund, Pschorr, Knorr, Willstätter (1890-), A. Pictet (1895-).

§ 3. **The Terpenes**—The chemical history of the "essential oils" formed by many plants and trees falls naturally into three divisions :—

(1) A preliminary period, in which crude essences were extracted from the plants, chiefly for their perfume; this extends to the remotest times, for the ancients knew how to make terpentine oil as well as oils of olive, almond, pear, etc. (most of which have been already dealt with). The alchemists added numerous others, such as those from rosemary, thyme, etc., and the group of herbal essences has continued to multiply steadily.

	Alkaloid.	*Discovery.*	*Molecular Formula.*	*Constitution.*	*Synthesis.*
Cinchona bark	Quinine	1820 Pelletier and Caventou	$C_{20}H_{24}N_2O_2$, 1838, Liebig	Strecker (1862), Skraup (1885), Königs (1880-), Miller and Röhde (1894)	—
,,	Cinchonine	1821 Pelletier and Caventou	$C_{19}H_{22}N_2O$, 1841, Laurent		
Strychnos	Strychnine	1818 Pelletier and Caventou	$C_{21}H_{22}N_2O_2$, 1839, Regnault	(Still unknown), Shenstone (1885), Zeisel (1885), Tafel (1890-), W. H. Perkin, jun. (1910)	—
Nux vomica	Brucine	1819 Pelletier and Caventou	$C_{23}H_{26}N_2O_4$, 1839, Regnault		
Pepper	Piperine	1819 Oersted	$C_{17}H_{19}NO_2$, 1840, Laurent	Anderson (1850), Regnault (1863)	1882 Rügheimer.
Hemlock	Coniine	1827 Giesecke	$C_8H_{17}N$, 1838, Liebig	Hofmann (1880-4), Ladenburg	1886 Ladenburg.
Tobacco	Nicotine	1686 as "oleum tabaci" / 1828 Posselt and Reiman	$C_{10}H_{14}N_2$, 1843, Barnal	Pinner (1890), A. Pictet (1895)	1904 Pictet.
Belladonna	Atropine	1831 Geiger, Hesse	$C_{17}H_{23}NO_3$, 1850, Planta	Ladenburg (1880-), Merling (1890-)	1901 Willstätter.
Cocoa-leaves	Cocaine	1859 Niemann	$C_{17}H_{21}NO_4$, 1860, Wöhler	Lossen (1865), Einhorn (1888-)	1885 Merck.
Opium	Morphine	1817 Setürner	$C_{17}H_{19}NO_3$, 1836, Pelletier	Anderson (1850-1880), Wright, (1860-70), Vongerichten and Schrötter (1884, showed these alkaloids to be phenanthrene derivatives); Freund, Pschorr, Knorr (1890-)	—
	Codeïne	1832 Robiquet	$C_{18}H_{21}NO_3$, 1838, Regnault		
	Thebaïne	1835 Thibournery	$C_{19}H_{23}NO_3$, 1870, Hesse		
	Papaverine	1848 Merck	$C_{20}H_{21}NO_4$, 1850, Merck		
	Narcotine	1803 Derosne	$C_{22}H_{23}NO_7$, 1831, Robiquet	Beckett and Wright (1875), Hesse (1870-), Freund (1890)	1909 A. Pictet. 1896 Liebermann.

(2) An intermediate period, extending from about 1810 to 1870, in the course of which many of the above oils were worked up and pure constituents obtained; yet, since structural chemistry was not at the time sufficiently advanced to be capable of explaining their constitution, the numerous investigators had in most instances to be perforce content with defining the molecular composition and the characteristic reactions of their various products.

(3) The period in which the constitution of terpenes has been seriously investigated; this did not commence till about 1890, but since that date an enormous mass of data has been and is being accumulated on the subject. Tilden (1880) showed that the addition-products of the terpenes with nitrosyl chloride or nitrous anhydride could often assist in determining their structure, and from 1890 onwards the work of Baeyer, Wallach, Wagner, Kannonikow, Kondakow, Bredt, Brühl, Barbier, Harries, Tiemann, Semmler, and their students, has been especially important in elucidating this very complicated problem. In 1894 a convenient nomenclature for the class of terpenes was arrived at, mainly by Baeyer and Wagner; the only other general statement it is possible to make here refers to the syntheses of members of the series, carried out by Baeyer in 1893 (from succino-succinic ester derivatives) and by W. H. Perkin, jun., since 1905 (mainly by the help of the Grignard reagent). Of these it is only the latter which has yielded terpenes identical with previously known natural products. The table on p. 143 summarizes the history of a few typical terpenes.

§ 4. **Sugars and other Carbohydrates; Glucosides**—The sugars form yet another class of compounds which have served to prove the capabilities of the modern structural theory of organic compounds for although numerous sugars were known before the latter took firm hold, their constitutions remained unfathomed until about 1885. Since then the whole maze of stereo-isomeric sugars has been cleared up and systematized, notably owing to the great work of Emil Fischer; and as

			Definitely Isolated.	*Early Workers.*	*Chief Modern Workers.*	*Synthesis.*
Naturally occurring	C_5H_8	Isoprene	1837 Bouchardat	Himly, Williams	Ipatiew and Wittorf, 1897	1898 Euler
	$C_{10}H_{16}$	Dipentene	1838 Himly	List, Deville	Wagner, Baeyer, Wallach	1905 Perkin
		Limonene	1841 Schweizer	Dumas, Pelouze	Tilden, Wallach	Perkin
		Sylvestrene	1877 Atterberg	—	Wallach	1910 Perkin
		Phellandrene	1841 Cahours	—	,,	1905 Harries and Johnson
		Camphene	1858 Berthelot	Tilden and Armstrong	Baeyer, Wagner, Wallach	—
	$C_{10}H_{20}O_2$	Terpin hydrate	1827 Voget	Wiggers, Kane	Kannonikow, Tiemann	1906 Perkin
	$C_{10}H_{20}O$	Menthol	Introduced early (from Japan)	Dumas, Kane	Beckmann, Brühl	1897 Beckmann [1]
		Citronellal	1889 Dodge	—	Tiemann, Barbier, Harries	—
	$C_{10}H_{18}O$	Terpineol	1849 Deville	Bertrand, Tilden	Stephen, Baeyer, Hesse, Wallach, Wagner	1906 Perkin
		Borneol	1841 Pelouze	Pelouze, Berthelot	Wallach, Haller, Kannonikow	1891 Haller [2]
		Citral	1888 Schimmel and Co.	—	Dodge, Tiemann, Semmler	1898 Tiemann
		Linalool	1882 Morin	—	Tiemann and Schmidt, Barbier	—
		Menthone	1882 Atkinson and Yoshida	—	Barbier, Baeyer and Villiger	1902 Leser
	$C_{10}H_{16}O$	Camphor	Introduced early from the East	Dumas, Pelouze, Kekulé	Kannonikow, Bredt, Baeyer	1895 Haller [3]
		Fenchone	1845 Bouchardat	—	Wallach	—
		Pulegone	1838 Kane	Beckmann	Barbier, Baeyer, Tiemann	—
		Thujone	1844 Schweizer	Bruylants, 1878	Semmler, Tiemann	—
	$C_{10}H_{14}O$	Carvone	1853 Völckel	Gladstone, 1863	Goldschmidt, Collie, Wallach	—
	$C_{13}H_{20}O$	Irone	1893 Tiemann and Krüger	—	Tiemann and Krüger	—
Artificia..		Ionones	1893-1900 Tiemann and Krüger	—	,,	All synthetic
	$C_{10}H_{16}O$	Carvenone	1893 Wallach	—	Baeyer, Tiemann, Semmler	—
	$C_{10}H_{16}$	Carvestrene 3 : 8(9)	1894 Baeyer	(Inactive Sylvestrene)	Semmler	1905 Perkin
	$C_{10}H_{18}$	Δ-2-menthadiene	1906 Kay and Perkin	—	(Optically-active)	Synthetic

a secondary result various artificial sugars have been produced in accordance with the indications of the theoretical formulæ.

We must first glance at some of the means which have served to characterize the otherwise not very well-defined members of the class. Their optical rotatory power (frequently showing mutarotation) has long been used as a test, and so has the reducing power which most of them exert on ammoniacal copper solutions (Fehling, 1849). Of their crystalline derivatives the phenylhydrazones and osazones (E. Fischer, 1884) are especially useful on account of their superior power of crystallization.

The most interesting part of their history, however, deals with the complicated syntheses which in a few master hands have led up to our present extensive knowledge of their configuration.

It was not until 1880 that the general nature of a sugar (aldehyde-alcohol) was realized (by Zincke), although in 1861 Butlerow had produced a sugar-like syrup, "methyleneitan," by alkaline condensation of trioxymethylene (polymerized formaldehyde). Similar syntheses were achieved by Loew, who obtained unfermentable "formose" by condensation of formaldehyde with lime (1886), and fermentable "methose" when magnesia replaced the lime (1889). E. Fischer's work commenced about 1884 with the investigation of the action of phenylhydrazine on sugars, and in 1887 he obtained "α-acrose" (afterwards shown to be *dl*-fructose) by the action of baryta on dibrom-acroleïn. In the meantime Kiliani developed methods for increasing the number of carbon atoms in a sugar by utilizing the hydrogen cyanide addition-products (1885-6), and Fischer showed in 1890 how the resulting oxy-acids (from the cyanhydrin hydrolysis) might be reduced to new sugars by sodium amalgam. By these means he completed the synthesis of *d*- and *l*- glucose, and *d*- and *l*-fructose and numerous other sugars, and by about 1894 had worked out with tolerable certainty the spacial configurations of the sixteen possible aldohexoses, the keto-hexoses, the eight possible aldopentoses, etc., and had deduced therefrom the configuration of *d*- and *l*-tartaric acids. Further

methods which tended to confirm all these theories were supplied by the reactions of Wohl (1893) and Ruff (1898), which permit of the degradation of a sugar to one containing one atom of carbon less in the molecule.

At the same time the constitution of the di- and tri-saccharides, such as cane-sugar or raffinose, has been partially cleared up, for in 1893 Fischer prepared alkyl ethers of the alcohols which were chemically analogous to the natural glucosides, and later it has appeared (Tanret, 1895; Perkin, 1902; E. F. Armstrong, 1903) that the poly-saccharides are constituted similarly to the synthetic glucosides, and are, therefore, condensation-products or "mixed ethers" of the different mono-saccharides (hexoses).

The structure of other carbohydrates—those of the formula $(C_6H_{10}O_5)_n$, where n is at present unknown, but certainly very large—has not yet been arrived at, and it would seem that it will remain an unsolved problem for some time to come.

We proceed to the usual historical summary (p. 146) of the class we have discussed, adding also a list of the most interesting natural glucosides (or sugar ethers). The existence of certain natural hydro-aromatic sugars, such as inosite (Scherer, 1850) or quercite (Hofmann, 1877), should not be overlooked.

§ 5. **Amido Acids, Proteins, and Purines**—The alkaloids and the terpenes are exclusively vegetable substances, the sugars occur chiefly in the vegetable, but also in the animal kingdom; the last group which remains to be considered is common to both, but plays an exceedingly important part in animal metabolism. This series, comprising organic bodies containing one (and usually several) groups of the type —NH . CH_2 . CO—, has been persistently investigated for nearly a hundred years, but at present, although it may be said that a general knowledge of its members has now been attained, there remain many of its naturally-occurring derivatives whose constitution has not been unravelled, and still

Class.	*Sugar.*	*Discovery in nature.*	*Synthesis.*
Biose	Glycollic aldehyde	Artificial	1894 Fenton.
Triose	Glyceric aldehyde	,,	1887 E. Fischer.
Tetrose	Erythrose	,,	1899 Wohl ; 1899 Ruff.
Pentose	*l*-arabinose	1869 Scheibler	1893 Wohl.
,,	*l*-xylose (wood sugar)	1886 Koch.	1900 E. Fischer and Ruff.
Hexose	*d*-glucose (grape sugar)	Very early times	1890 E. Fischer.
,,	*d*-mannose	1861 Besanez	1903 Neuberg and Mayer.
,,	*d*-galactose	1856 Dubrunfaut	1895 E. Fischer.
,,	*l*-fructose (fruit sugar)	1847 Dubrunfaut	1890 E. Fischer.
Disaccharide	Cane sugar (*d*-glucose + *l*-fructose)	Known very early	1899 Marchlewski.
,,	Milk sugar (*d*-glucose + *d*-galactose)	1615 Bartoletti	—
,,	Maltose (*d*-glucose + *d*-glucose)	1847 Dubrunfaut	—
,,	Isomaltose	Artificial (1st member)	1890 E. Fischer.
Trisaccharide	Raffinose (*d*-glucose + *d*-galactose + *l*-fructose)	1884 Ritthausen	—

Glucosides.	*From*	*Discovery.*	*Chief workers.*
Quercitrin, $C_{21}H_{22}O_{12}$	Rhamnose and quercetin (cf. p. 145)	1810 Chevreul	Liebermann, 1879 ; Dunstan and Henry, 1898.
Phloridzin, $C_{21}H_{24}O_{10}$	Glucose, phloroglucin, phloretic acid	1835 Koninck	Stas, 1840; Schiff, 1880; Fischer, 1888.
Amygdalin, $C_{20}H_{27}NO_{11}$	$(Glucose)_2$, mandelonitrile	1837 Liebig and Wöhler	Wöhler, 1848; Fischer, 1895.
Salicin, $C_{13}H_{18}O_7$	Glucose, *o*-oxybenzylalcohol	1839 Piria	Perkin, 1868; Hesse, 1875.
Digitalin, $C_{29}H_{46}O_{12}$	Glucose, galactose, and digitalin	1851 Walz	Kiliani, 1891-1898.
Myronic acid, $C_{10}H_{19}NS_2O_{10}$	Glucose, allyl mustard oil and potassium hydrogen sulphate	1863 Will	Hofmann, 1868; Gerlich, 1875.

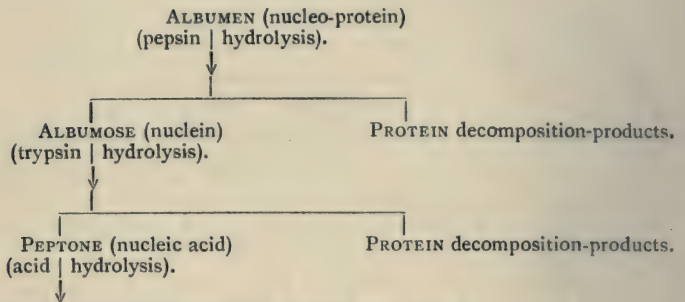
more whose supposed structure has not been confirmed by synthesis.

The first indications of the important natural rôle of substances containing this group came as early as 1820, when Braconnot obtained a substance "glycocoll" by boiling glue with dilute acids. In the ensuing thirty or forty years various other compounds, which bore more or less chemical resemblance to glycocoll, were prepared from meat extract, milk, bile and similar animal juices. Liebig, Wöhler, Liebreich and others subsequently found that the cause of the similarity lay in the fact that the creatine, tyrosine, asparagine, serine (to name only a few of the compounds in question) were all derivatives of the amido-acids. This naturally led to synthetical work on the amido-acids, commenced by Strecker about 1860, and continued by numerous chemists down to Erlenmeyer, Curtius, and especially Emil Fischer, the present-day workers in this branch.

In this way it was soon found (cf. the table which follows) that a number of these animal decomposition-products were either amido-acids (e.g. glycocoll, tyrosine), cyclic anhydrides of amido-acids (creatine, betaïne), amides of amido-acids (asparagine, urea, guanidine), or more complicated amido-acid derivatives, such as cystine, tryptophane, or proline (some of the most recently added members). Moreover, the ptomaines or "corpse alkaloids," poisonous products of animal decay, were also found to be closely related to the above (Selmi, 1872), being simple aliphatic diamines.

More important than all this, however, are the efforts which have been made with no small success to trace a connexion between such chemically simple end products of decomposition and the complicated components of living bodies known as albumens. Various workers have shown within the last twenty years that the molecular magnitude of such substances (e.g. casein, hæmoglobin, etc.) is very large, and cannot fall short of 16,000 in most cases; but no precise conception of albuminoid struc-

ture was arrived at until Fischer turned his attention to the problem about 1900, having solved those of the sugars and of the purines (to which we shall shortly refer). His work is too extensive to recount in detail, but it may be summed up in the diagram which he has succeeded in drawing up to show the successive decompositions of an albuminous substance :—

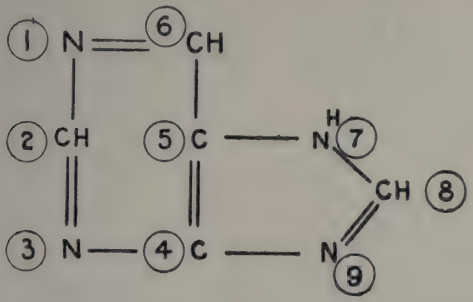


From these protein or polypeptide decomposition-products Fischer has isolated definite compounds of the general structure $NH_2[CH_2.CO.NH]_n.CH_2.COOH$, and, on the other hand, he has synthesized chemically similar substances (although of less molecular weight) from simple amido-acids by a variety of methods, obtaining in the latest instance an octadecapeptide containing fifteen glycocoll and three leucine groups (1907).

He has thus shown the general nature of the proteins and, consequently, of the albumens.

For a number of years previous to the protein work he was engaged in consummating by decomposition, as well as by synthesis, the knowledge of another group of natural products such as caffeine, uric acid, xanthine, guanine (previously studied by Liebig, Strecker, Baeyer, and many others), all of which he

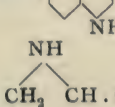
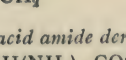
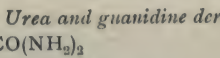
proved to be derivatives of a parent substance "purine,"

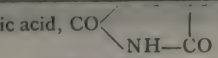
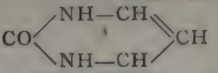
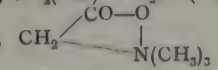


which he finally prepared (1898). This remarkable work (sugars—purines—proteins) is one of the most complete series of investigations on record in chemical history.

Since 1900 W. Traube has also contributed a number of independent syntheses of most of the purines.

In the following table the various natural amido-acid or amido-acyl products are grouped according to the order in which they have been discussed above:—

	Discovery.	*Other workers.*	*Synthesis.*
(*a*) *Fatty Amido-acids* :—			
Glycocoll, $NH_2 . CH_2 . COOH$	1820 Braconnot	Dessaignes, Strecker	1858 Perkin and Duppa.
Sarcosine, $NH(CH_3)CH_2 . COOH$	1847 Liebig (meat extract)	Schultzen, Strecker	1862 Volhard.
Alanine, $CH_3 . CH(NH_2) . COOH$	1850 Strecker	Kekulé, Limpricht	1850 Strecker.
Leucines, $C_4H_9 . CH(NH_2) . COOH$	1820 Braconnot	Cahours, Liebig	1855 Limpricht.
Taurine, $NH_2[CH_2]_2 . SO_3H$	1824 Gmelin (ox-bile)	Redtenbacher	1862 Kolbe.
(*b*) *Aryl or Heterocyclic amido-acids* :—			
Tyrosine, $C_6H_4(OH) . CH_2 . CH(NH_2) . COOH$	1846 Liebig (cheese)	Fischer	1883 Erlenmeyer.
Phenylalanine, $C_6H_5 . CH_2 . CH(NH_2) . COOH$	1881 Schultze (lupins)	Fischer	1882 Erlenmeyer.
Tryptophane,	1896 Kossel	Hopkins and Cole	1907 Ellinger.
Proline, 	1899 Fischer	Aders	1901 Fischer.
(*c*) *Amido-acid amide derivatives, etc.* :—			
Asparagines, 	1805 Vauquelin (laevo) 1886 Piutti (dextro)	Liebig, Kolbe	1887 Piutti and Körner.
Serine, $CH_2(OH) . CH(NH_2) . COOH$	1865 Cramer	Baumann	—
Cystine, $S_2[C(CH_3)(NH_2) . COOH]_2$	1810 Wollaston	Dewar and Gamgee	—
(*d*) *Urea and guanidine derivatives* :—			
Urea, $CO(NH_2)_2$	1773 Rouelle (urine)	Liebig, Knop, Kjeldahl, etc.	1828 Wöhler.
Alloxan, 	1818 Prout	Baeyer	1883 Baeyer.

Parabanic acid, 	1838 Liebig and Wöhler	Strecker	1872 Ponomarew.
Uracyl, 	—	—	1901 Fischer.
Guanidine, $NH = C(NH_2)_2$	1861 Strecker	Bouchardat	1866 Hofmann.
Creatine, $NH = C(NH_2) . N(CH_3) . CH_2 . COOH$	1834 Chevreul (meat extract)	Liebig	1869 Volhard.
(e) Betaïnes :—			
Choline, $CH_2(OH) . CH_2 . N(CH_3)_3 . OH$	1862 Strecker (bile)	Baeyer	1868 Wurtz.
Betaïne, 	1869 Scheibler (sugar beet)	Griess, Jahns	1869 Liebreich.
(f) Ptomaines :—			
Putrescine, $[CH_2]_4(NH_2)_2$	1885 Bocklitch	Ellinger	1886 Ladenburg.
Cadaverine, $[CH_2]_5(NH_2)_2$	1885 Brieger	Baumann	1886 Ladenburg.
(g) Purines :—			
Uric acid [2.6.8. trioxypurine]	1776 Scheele	1793 Fourcroy 1826 Liebig and Wöhler 1863 Baeyer 1875 Medicus (formula)	1882 and 1887 Horbaczewski. 1888 Behrend and Roosen. 1897 E. Fischer. 1901 Traube.
Xanthine [2.6. dioxypurine]	1817 Marcet	1834 Liebig and Wöhler	1897 E. Fischer. 1900 Traube.
Caffeine [1.3.7. trimethylxanthine]	1821 Pelletier (coffee) 1838 Jobst (tea)	1881 Fischer	1899 E. Fischer. 1901 Traube.
Theobromine [3.7. dimethylxanthine]	1842 Woskresorski (cocoa)	1865 Strecker 1881 Fischer	1897 E. Fischer. 1900 Traube.
Guanine [2. amino-6. oxypurine]	1844 Unger (guano)	1861 Strecker	1900 Traube.
Adenine [2. amino-purine]	1885 Kossel (pancreas)	1897 Fischer	1898 E. Fischer.

§ 6. **Fermentation and Enzyme-Action**—We will conclude this chapter with a reference to the part played by certain bacteria and imitated by a number of lifeless substances in promoting many chemical actions, and usually denoted by the phrase fermentation. The formation of wines from grape-juice was ascribed to this process centuries ago, and van Helmont went so far as to say that "fermentation" was the principal cause of all organic processes, but it is doubtful whether he used the terms with anything approaching their modern signification. At all events the real nature of vinous fermentation was not appreciated in his day, for it was not until 1680 that Becher showed that sugar must be present, while the fact that the alcohol and carbonic acid come directly from this sugar was only revealed by Lavoisier in 1783. During the next half-century, however, numerous other cases of ferment action came to light (lactic acid, higher alcohols, etc.), and it was also realized that many of the chemical reactions going on in animal bodies are maintained by the agency of ferments.

Theories were not wanting to "explain" the mechanism of the process; we may refer to the Berzelius-Mitscherlich "contact" theory (1834-6) and to Liebig's "vibration" theory (1839) which assumed that ferments were in a state of continual molecular oscillation which induced a similar vibration (causing molecular disruption) in certain other molecules. Such hypotheses had little if any experimental support, and indeed a discovery made by Cagniard de la Tour three years prior to Liebig's hypothesis pointed to a very different explanation, for it was found that the yeast cells present during sugar fermentation actually multiplied in the process. Later on it was observed that not all the known ferments grew in this manner, but only definite members of the class, but little of importance was settled with regard to the subject until in 1855 Pasteur collated all the known facts, and after much investigation elaborated his "vitalistic" theory, declaring that all real fermentations were the results of the action and multiplication of living or-

ganisms. This, while giving a partial insight into ferment action, did not explain the processes involved in the case of those ferments such as emulsin (1830, Robiquet), ptyalin (1831, Leuchs), diastase (1834, Payen and Persoz), pepsin (1835, Schwann), invertase (1870, Liebig) and "inorganic ferments" (colloidal platinum, etc.) which are not made up of living cells at all; all these were set by Pasteur in a separate class—the enzymes or unorganized ferments.

Much work has since been undertaken on this very difficult problem, but although Pasteur's generalizations have held their place, it must be admitted that there is much that is arbitrary and unsatisfying in his explanation. Again, Buchner has shown (1896) that sugar is fermentable by a juice present in yeast, but not containing any living cells, and so it would seem that possibly the vitalistic theory may yet give way to a more general solution embracing both organized ferments and enzymes.

Other recent students include Knap, Nef, Meissheimer and Emmerling; the latter showed in 1901 that in some cases enzyme action is reversible, i.e. the same product which decomposes a glucoside, for example, may under given conditions bring about its synthesis from its hydrolysis products.

The mechanism of fermentation was first studied from a physico-chemical standpoint by Wilhelmy in 1850; later workers include O'Sullivan (1885-1900), Adrian and Horace Brown (1892-), and E. F. Armstrong (1904). The general result has been that, although at one time apparent exceptions were encountered, fermentation proceeds strictly according to the law of mass-action, and conforms just like any other chemical change to the laws of chemical kinetics.

CHAPTER IX

THE APPLICATION OF CHEMISTRY TO MANUFACTURES

To omit any reference to the part chemistry has played in engineering, agriculture, dyeing and many other equally conspicuous aids to what is called civilized existence would be to render a very one-sided record of chemical history. On the other hand, it is obviously impossible to chronicle all the technical improvements made in manufacturing processes, more particularly within the last hundred years. We will therefore refer briefly to the more notable applications of pure chemistry to " the arts," ranging from the earliest (the purification of gold, silver and other metals easily obtained from their ores) to the most recent products of civilization (the use of electricity and petrol ; the invention of " high " explosives).

The parts of the globe noted for excellence of technical work have extended at different periods from eastern to western hemispheres. The ancient oriental peoples are the earliest that we can say with certainty applied chemistry (albeit in an empirical manner) to manufactures (e.g. Chinese pottery and Egyptian colouring). During the Middle Ages, Italy and France were the most prominent countries in this respect, and later came the modern supremacy of England. Most recently there has been witnessed a remarkable development of industrial operations in Germany, which has given rise to much pessimistic talk in England. But if British manufacturers show more readiness to adopt the latest technical devices, and give adequate support to the facilities now available for the instruction of their

workers, little fear need be entertained as to whether our country can "hold its place". Finally, the modern system of transit, etc., has modified the location of factories, so that whilst in some cases raw material is brought to the centres of civilization for fabrication, in many others the ore, crop, or whatever it may be, is worked up in distant parts of the world close to its natural source.

Turning to the purely scientific side of the subject, it will be well to point out how, especially of recent years, purely theoretical researches have assisted the manufacturer. We may do this best by giving a few concrete examples:—

(1) Le Chatelier's work on the "phases" and the thermal conditions prevailing in the blast furnace.

(2) The same physical chemist's research on the conditions of equilibrium of the reactions $CaCO_3 \rightleftarrows CaO + CO_2$ and $CO_2 \rightleftarrows CO + O$.

(3) The elaborate electrochemical and thermochemical theories upon which the processes for the "fixation of atmospheric nitrogen" (§ 3) are based.

(4) The difficulties (only overcome by years of research) in the practical application of the sulphuric acid "contact process".

(5) Syntheses of various organic compounds have provided means for supplying many products more cheaply (alizarin, indigo, etc.).

We will now proceed to give a more detailed account of this practical application of results obtained in the laboratory.

§ 1. **The Preparation of Useful Elements. Metallurgy**—Taking first the larger branch—metallurgy—of this division, we may divide modern practical methods as follows:—

(*a*) *Those which are simply improvements of older fundamental principles.*

(*b*) *Those which involve entirely new processes* (*in most instances the application of electricity*).

(*a*) The principle of the smelting of a few ores, such as those of lead, tin, copper, and mercury, remains the same to-day as

when directions for making these metals were recorded by Greek and Roman philosophers. These directions were naturally simply of the nature of recipes, the explanation of the different processes being but imperfectly understood all through the alchemical and phlogistic periods. The alchemists, however, knew sufficient to enable them to use a rough sort of analysis as a check on the purity of their products, the first advice on the subject of assaying appearing in the works of Agricola and Libavius.

Modern modifications have consisted here in the use of a "wet process" (Hunt and Douglas) and an electrolytic precipitation process (Elsmore, Siemens, and others) for copper, methods of desilverizing lead (Pattinson, Parkes), and economic improvements in the metallurgy of some other elements, such as zinc (Marggraf, Stromeyer).

Among elements which are still obtained by processes centuries old we may mention mercury, sulphur, bismuth, and tin.

The metals of the platinum group were first isolated on a commercial scale by Cock (1800-1808) in the form of impure platinum; Deville and Debray constructed a furnace for the fusion of these metals and Matthey showed how to separate and purify them.

Before dealing with the iron industry (the most important of this section), we will recall the introduction of electro-plating by De la Rive in 1836 and Jacobi in 1839, a method which was extended during the next generation to the cases of copper, silver, gold, nickel, and manganese, amongst others.

The manufacture of iron and steel went on by the old Catalan and allied processes until in 1784 Cort introduced the puddling process for wrought iron; another important improvement was the substitution of hot for cold air in the blast for the furnaces (Neilson, 1828). Between 1856 and 1867 the Bessemer process for converting cast iron to steel was perfected; contemporaneously another method was introduced by Siemens and Martin. These were improved upon by the Thomas-Gilchrist

process (1878-80); Wagner has shown how the slag from this process, rich in phosphates, may be utilized agriculturally as a manure. Such is a bare outline of one of the most important British industries; other points of scientific interest include the researches of Bunsen and Playfair on the composition of furnace-gases, and the utilization of the spectroscope by Bradge and Roscoe to detect the end point of the reaction in the Bessemer process.

(*b*) The newer methods of element manufacture apply as a rule to elements difficult to isolate from their compounds and consist mainly of electrolytic processes and processes involving extremely high temperatures.

The first type includes the modern manufacture of the alkali and alkaline earth metals, magnesium, aluminium, etc. Of these, the alkalies were formerly made by violent reduction processes; calcium, strontium,and barium had only been obtained impure by the action of sodium amalgam on their salts, and the rest were made by fusing their chlorides with sodium (Wöhler, Deville). The case of the alkali elements is particularly interesting; Davy's electrolytic isolation of these was regarded as of purely theoretical interest, and Gay-Lussac and Thénard tried to manufacture sodium commercially by heating iron with fused caustic soda. Later, in 1823, Brunner showed how potassium resulted from the ignition of an intimate mixture of the carbonate and charcoal; Deville improved upon this by igniting a paste made of soda and chalk with oil. Such methods were comparatively costly, but the electrolysis of the fused chloride or hydrate on a commercial scale by Castner (1890) furnished a cheap means of preparing the pure elements. A further modification is the electrolysis of the aqueous alkalies with a mercury cathode, with which the liberated element at once amalgamates. The alkaline earth and other elements are all prepared at the present day by electrolysis of their fused chlorides (in the case of aluminium, electrolysis of a solution of bauxite AlO(OH) in fused cryolite AlF_3, 3NaF).

Reduction of refractory oxides at high temperatures has been carried out of recent years by Moissan (a mixture of charcoal and oxide of uranium, tungsten, manganese, chromium, silicon, or titanium being heated in the electric furnace, 1893-6), by Readman and Parker (phosphorus from phosphates, sand, and coke in an electric furnace, 1902), and by the "thermite" process of Goldschmidt (1898), an intimate mixture of aluminium powder and an oxide of iron, nickel chromium, manganese, etc., which on ignition by a thermo-detonator yields the metal and alumina with evolution of much heat.

The manner in which of late years manufactories for the production of the rarer elements and compounds have sprung up is noteworthy; we may instance those for the rare earth oxides and elements (for Welsbach "mantles," etc.), as well as the new factory in London for uranium and radium compounds. The use of potassium cyanide in gold and silver extraction is a metallurgical improvement which has now been applied for many years.

The technical history of a few gaseous elements is also interesting; chlorine, for example, was manufactured on modern lines by Weldon (1868) from pyrolusite, an important addition being the Weldon-Péchiney method of recovering the manganese (1882); another method (decomposition of HCl by heated copper salts) was devised by Deacon (about 1880), while at the present time a large amount of chlorine is produced in the Kellner-Castner electrolytic process for caustic soda from brine (see § 2).

Finally, nitrogen and oxygen are now exclusively prepared by the fractional distillation of liquid air, the older methods of depriving air of oxygen by barium oxide (Brin, 1881) and recovering the oxygen from the barium peroxide formed, having failed to compete successfully with the newer process.

§ 2. **The Alkali, Sulphuric Acid, Vinegar and similar Industries**—We have next to deal with a number of industries which usually go by the name of "chemical manufactures," and

we may take the "soda industry" as one of the most important instances. Sodium and potassium carbonates were made in olden days by incinerating sea-shore plants ("barilla"), but towards the close of the phlogistic period search was made for a better method. The clue to this improvement was supplied by Guyton de Morveau in 1782, who showed that soda is formed when Glauber's salt is heated strongly with coal and iron. Leblanc (1787-91) based his process upon this observation, preparing the sulphate from common salt and then heating it with coal and chalk, finally obtaining the carbonate from this by washing with water. The system was first worked in England by Muspratt in 1824.

Some fourteen years later Dyar and Hemming took out a patent for obtaining soda crystals from common salt by the action of carbonic acid in the form of ammonium carbonate. This was improved by Solvay in 1861 and adopted in 1874 in England at Brunner, Mond & Co.'s works. Finally, Hargreaves and Bird (1896) have introduced an electrolytic method for soda production from salt, using a special electrode permeable to sodium ions, but not to brine, and supplying a stream of carbon dioxide externally to the electrodes whereby the product obtained is soda crystals or simply caustic soda as required.

These two last methods have cheapened soda-fabrication to such an extent that the Leblanc process is now only valuable for its bye-products—hydrochloric acid, first collected as an aqueous solution from the conversion of the salt to sulphate by Gossage (1836), and sulphur and sulphides of calcium, utilized by the recovery processes of Chance (1888) and others.

Caustic soda itself used to be made technically (from 1850 onwards) by "causticising" soda solutions with lime, filtering from chalk and concentrating. About 1885 the Castner-Kellner process of electrolysing brine with a movable mercury cathode came into operation; the mercury is first made to act as cathode and then decomposed by water by mechanical oscillation. Later

processes have all been modifications of the electrolytic principle.

We have just indicated the chief source of hydrochloric acid; of the other two most important mineral acids there is little of note in the preparation of nitric acid (for which Boyle gave the first technical directions) except the recent electrical methods mentioned in the next paragraph. The means of producing oil of vitriol, on the other hand, have varied a good deal. First manufactured by the Nordhausen method (distillation of green vitriol) in alchemical times, a great improvement was effected in its fabrication by Roebuck (1746) at Birmingham, Gay-Lussac (1824), and Glover (1841), who evolved between them the "lead chamber process". More recently this has been in part superseded by the "contact process," in which sulphur dioxide and oxygen unite by the catalytic action of finely-divided platinum. A patent covering this method appears under the name of Philips as far back as 1831, but it was not till about 1875 that a practical paying process was devised (Winkler, Knietsch). Since 1900 the Badische Anilin und Soda Fabrik have improved it in various directions, such as eliminating traces of arsenic (which "poisons" the platinum) from the mixed gases, and employing sulphates of cerium, lanthanum, and other rare earth metals as additional catalysts.

Of other inorganic chemicals produced in large quantities "chloride of lime" (bleaching powder) may be mentioned. The commercial process was designed by Thénard in 1799 and carried out by Tennant & Co. in England. About the same time Berthollet introduced his "Eau de Javelle" (aqueous sodium hypochlorite). It may be remarked that the constitution of bleaching powder was quite unknown till about 1835, when Balard suggested the formula $CaCl(OCl)$.

Turning to the more common organic products, we find that alcohol ("spirits of wine," "aqua vitæ") has been obtained from wines from the earliest times by simple redistillation, though in this way it never attained a strength of more than

92 per cent. During the past century, and more particularly since about 1875, when the phylloxera began to increase its ravages amongst vines, beet-sugar and potatoes have been the source of most of the alcohol supply. Still-heads for improving the fractionation process are due to Argand, Adam, and Blumenthal; Gay-Lussac systematized alcohol analysis ("alcoholometry") in 1824.

The essences or ethereal oils (in many cases ethyl esters) have always formed a branch of chemical industry, but as the improvements deal chiefly with mechanical appliances for expressing or distilling the different plant-juices, we will merely remark here that Vaudin introduced vacuum distillation into essence works in 1879, and that since 1885 Schimmel & Co. have been the pioneers in this branch of the technical science.

Vinegar used to be made from alcohol by Boerhave's fermentation method (1720), known as the "slow" or "Orleans process"; in 1823 Schützenbach and Wagemann introduced the German or quick vinegar process. Acetic acid itself was first made on a large scale by distillation of wood by the patents of Kestner and of Halliday (1848), the purification of the pyroligneous acid by lime being due to Mallerot.

Cane-sugar came originally from Asia and was introduced to Southern Europe and Africa by the Moors; thence it was transferred to the Central American islands by the Spanish and Portuguese colonists, and at the present day it is a decaying industry in those regions, owing to the introduction of beet-sugar. The presence of sugar in beet-juice was discovered by Marggraf in 1747, but the first technical means of extracting it were found by Achard in 1779. The first factory was started in France in 1796, and until about 1836 the bulk of the beet-sugar came from French soil; since then, however, Austria-Hungary, and especially Germany, have taken the lead. Filtration of the raw juice through mineral charcoal was introduced by Figuier (1811), evaporation of the syrup under

reduced pressure by Howard (1813), and the modern diffusion-process by Roberts in 1866.

Finally, soap was made by the action of alkalies on fats by the Greeks and by even more remote peoples. Its passage westward is marked by the Spanish and Italian soap works of the eighth and those in France of the twelfth centuries. Resin soaps date from about 1845. For the last fifty years or more the glycerine simultaneously resulting from the saponification has been worked up as a bye-product; since 1870 it has been purified usually by distillation with super-heated steam, and in a vacuum. At about that date, too, the fat-hydrolysis began to be conducted under pressure. We must not omit the fact that Chevreul's remarkably thorough researches on fats (about 1810) have been of the greatest benefit to technologists.

§ 3. **Some recent Electro-Technical Methods**—Besides electrolysis and the isolation of refractory elements in the electric furnace there has been a notable development of late years of electrical methods for producing artificial nitrogenous manures and commercially useful metallic carbides, and therefore a brief summary of these may be of interest. Dealing first with the "fixation of nitrogen," it should be observed that Berthelot in 1855 accurately predicted the four most valuable lines along which to prosecute research in this direction. Within the last few years atmospheric nitrogen has been brought into combination as follows by processes more or less applicable on the large scale:—

(*a*) *As Oxides of Nitrogen.*—Lefebre (1859) and Meissner (1863) found that "sparking" air mixed with oxygen was of little use, the products re-dissociating as soon as formed. Crookes (1892) succeeded in obtaining nitric oxide by the high tension arc, and practicable commercial processes were at length devised by McDougall and Howbres (1900) and by Birkeland and Eyde (1903) in Norway, who use a complicated arc distorted electromagnetically and absorb the nitrogen oxides in lime.

(*b*) *As Ammonia.*—Mackay and Hutchison (1894) heated coal and potassium carbonate in a current of air, and decomposed the resulting cyanide by steam; Kaiser (1900) devised a process whereby calcium

hydride CaH_2 was transformed to the nitride Ca_3N_2 by heating in nitrogen, and this, heated in hydrogen, gave ammonia and the hydride again. De Hemptinne (1900) combined nitrogen and hydrogen by the spark or silent discharge at low temperatures, and Schlutius (1903) submitted "Dowson gas" (from air and steam over red-hot coal) to the silent discharge in presence of moist platinum.

(*c*) *As Cyanides.*—Farmes (1842) and Bunsen and Playfair (1847) found that at high temperatures alkalies and coal yielded cyanides; the Ampère Electric Co. (1903) and N. Caro (1906) pass nitrogen over a mixture of coal and barium or calcium carbonates in the electric furnace, thereby obtaining either barium cyanide $Ba(CN)_2$ or calcium cyanamide Ca : N . C : N.

(*d*) *As Nitrides.*—Mehrer heats oxides of boron, silicon or magnesium with coke in the electric furnace; the resulting nitrides readily yield ammonia with the moisture in the soil.

A contributing cause to these developments has doubtless been the knowledge that the mineral supplies of nitrates and other nitrogenous manures are limited and will certainly sooner or later become exhausted.

Of technically valuable carbides we may notice that of calcium, used to generate acetylene, first prepared by Wöhler (1862) by heating coke and an alloy of zinc and calcium, then by Moissan (1892) by calcining lime and coal at 3000° C. in the electric furnace. Moissan first obtained it pure in 1894. Silicon carbide ("carborundum") is also useful by reason of its hardness; it was first prepared by Moissan in 1893 (from silica and carbon).

§ 4. **Glass, Earthenware, and Cements**—These indispensable aids to modern civilization were all known before our era. Glass, which is manufactured to-day in many different forms, soft or hard, ornamental or useful, was first made, as far as is known, by the Egyptians (about 3000 B.C.). After varying from Rome to Constantinople, the seat of the industry became fixed for a considerable period in Northern Italy, where considerable advances were made in the art of glass-colouring, notably by the Florentine Neri (*c.* 1640). Glass has been manufactured quite generally in the Western European

countries since the seventeenth century. Of improvements in its fabrication, we may note the introduction of plate glass by de Nehan in 1688 (an improved process was devised by Pélouze in 1856), the substitution of sand projected under great pressure for hydrofluoric acid in engraving by Tilghman in 1870, and the advances effected by Siemens in the fusion process. Modern glass usually contains much more soda and correspondingly less lime than the older varieties. In 1869 Emmerling and Bunsen contributed some important work on the solvent action of water, acids, alkalies, and various salts on specific kinds of glass. The phenomenon of devitrification was first observed by Réaumur, about 1770.

Earthenware, again, was certainly used by the Chinese as well as by the Egyptians, but pottery impermeable to water has only been known since the eleventh century of our epoch, while the finer kinds of earthenware first appeared some 300 years later (the Moors in Spain, and the Italians, notably L. della Robia, 1411-1430); Palissy's great improvements in this branch took place about 1550. Porcelain was introduced from China about 1600, and a century later Morin made efforts to reproduce the Chinese excellence at Saint-Cloud; Wedgwood was at the zenith of his fame as a potter about 1750, and a decade or so later the famous Sèvres porcelain was first manufactured, owing to the efforts of Réaumur, Macquer, and others. In 1800 Spode commenced the custom, which has remained practically confined to English potteries, of substituting bone ash for a part of the kaolin or clay otherwise used. Of recent years Seger (1892) has still further improved the manufacture of earthenware, and much research has been carried on with the aim of elucidating the chemical structure of clays.

There is not a great deal of interest attaching to the history of cements; four general classes are recognized at the present time: lime, Roman cement, Portland cement (which is an artificial mixture approximating in composition to the older Roman kind) and hydraulic cements. The latter require the

addition of water to make them "set"; they were introduced about 1800 in England and contain lime with an abundance of alumina. Improvements in hydraulic mortars were made, notably by Winkler and Knapp, a few years ago; theories of the manner in which cements "set" by atmospheric action have been discussed during the past quarter of a century by Le Chatelier, Newberry, Rebuffot, and others.

§ 5. **Paper, Matches, Heat, and Light**—The use of cotton fabrics for paper manufacture did not commence to supersede the old papyrus and parchment in Europe till the eleventh century, although in China it was used long previously. The oldest mark on cotton paper is dated A.D. 1050. Paper manufacture became general in France and Bavaria about 1400, but all paper in England was imported until 1588. In 1750 Baskerville produced "vellum paper". Later improvements may be summarized as follows: the introduction of machinery (1803), improved by Dickinson (1809); production from different trees (palms, bananas, etc.) (1839-1851); production from wood-pulp or straw (1846), rendered practicable by the processes of Wölter (1867), Aussedot, and Tessié. Paper used to be bleached by chlorine gas, but of late years a better and safer electrolytic method has been adopted.

The first matches, other than the primitive flint and tinder, were made of a mixture of potassium chlorate and sulphur ("chemical tinder," 1807), which was dipped in oil of vitriol to effect ignition. Their use was not, it is believed, very extended! In 1833 Romer and Moldenhauer introduced phosphorus matches, while the original form of the modern safety-match, in which red phosphorus is used (and usually only on the prepared surface of the box), dates from 1848. Of late years legislation has in some degree helped to eliminate the older forms of poisonous matches, containing yellow phosphorus.

A very important modern industry is that of india-rubber (first introduced into Europe in 1736), the raw material emanating chiefly from Para, Peru, Central America, and the

Congo. The most interesting development, chemically speaking, is the process of vulcanization by means of sulphur, discovered by Goodyear in 1839. Many attempts have been made to effect its synthesis, and Harries appears recently to have succeeded.

The ancient source of heat for domestic purposes was wood, and although coal was known to the Greeks and Romans it was not greatly used as a combustible until towards the middle of the eighteenth century, when the introduction of machinery into the arts created a demand for a cheap fuel. Coke was first manufactured in 1769. It is almost needless to point to the uses made of coal-gas and electricity for heating purposes during the last fifty years, but we may enumerate a few gas fuels used for technical purposes at the present day, such as "producer gas" (CO and N_2, by partial burning of coal in insufficient air), "water-gas" (CO and H_2, by blowing steam over red-hot coke; a very hot flame, useful technically), "mixed gas" (CO, H_2 and N_2, by blowing air and steam over burning coal; cheap and hence useful in small works), and "Dowson gas," which is practically synonymous with the last.

The problem of illumination has several times had a curiously beneficial effect by indirectly throwing light upon purely theoretical questions. A commission to improve the means of lighting the Paris streets turned Lavoisier's attention to the subject of combustion, and again, Dumas' efforts to elucidate the nature of annoying fumes emitted by chlorine-bleached candles at a French state function led to his discovery of substitution in organic compounds. Of general inquiries into the nature of luminosity, Sir H. Davy's (inventor of the miner's safety-lamp) and Frankland's have been most useful. With regard to specific illuminants, candles made from tallow (stearic or palmitic acids from fat by lime or, later, sulphuric acid) and subsequently wax (solid paraffins and plant waxes) come first in chronological order. Oils of varying kinds were also used—at first aromatic, scented oils, and in more modern times, petroleum from

Russian or American wells. At present the distillation of petroleum ranks second in importance to that of coal, and yields (in descending order of volatility) gasolines for motor-engines, petroleum ether, naptha or ligroin for lighting and solvent purposes, machine-oils, and finally, "heavy oils," semi-solid greasy materials useful as lubricants. Caucasian petroleum is made up mainly of hydroaromatic hydrocarbons, American of aliphatic or paraffin hydrocarbons.

Finally we come to coal-gas, introduced in 1792 by Murdoch, first made on a large scale six years later, and used in lighting London streets by Winsor in 1813. Experiments were made intermittently and unsuccessfully from 1800 to 1850 to use cheaper forms of gas, such as oil-, peat-, or water-gas. Technical improvements in coal distillation continued to be made until about 1880, but since that date no fundamental change has been made in the method as perfected by Lunge, which, in its most efficient form, permits of the utilization of "raw gases" (for heating), coal-gas, gas-liquor (source of ammonium salts and sulphides), tar (to be re-distilled) and coke residue.

The distillation of the coal-tar (first carried out by Clayton in 1738 and later, in France, by Lebrun in 1786) has grown to be a most important industry; the tar itself is used for protecting iron, wood, ships, etc., against air and water, as an artificial asphalte (mixed with sand), and in various other ways, while its distillation products include benzene and many other aromatic hydrocarbons of boiling-points ranging from 80° to 300° C., and technically important substances (especially to the dye industries) such as phenol, naphthalene, anthracene, pyridine, carbazole, and a host of others.

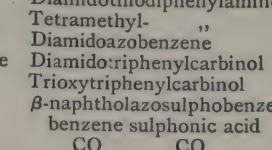
The introduction of rare earth oxides in the form of "incandescent" mantles is due to Welsbach (1885); improvements both in the composition of the film of oxide and in its mechanical arrangement continue to appear.

§ 6. **Dyes** — Indigo, madderwood and a few mineral colours such as minium, cinnabar, rouge, orpiment, realgar and

galena were known to the ancients, judging from their writings (e.g. Pliny). There is not much to record during the alchemistic period, though isolated workers, such as Glauber, occasionally investigated dyeing processes. The use of mordants (alum, iron salts) became known during this epoch, but their precise mode of action is even now imperfectly understood. Macquer was the first chemist to look into this problem (1795). A table showing the chief mineral and other dyes manufactured at the opening of the modern era may be useful :—

Pigment or Body Colour.	*Chemical Nature.*	*Artificial Preparation.*
Cobalt blue (smalt)	—	1650 Schürer (fusion of glass and cobalt residues)
Prussian blue	$Fe_4[Fe(CN)_6]_3$	1704 Diesbach
Alizarin	—	1750 From madder plant in Europe
Zinc white	ZnS	1790 Courtois
White lead	$Pb(CO_3)_2$ (basic)	1801 Thénard
Schweinfurt green	$Cu(C_2H_3O_2)_2, 3Cu(AsO_2)_2$	1814 Sattler
Ultramarine	From sodium silicates and sulphur	1828 Guimet; Gmelin (formerly from lapis-lazuli)

The more recent history of organic dyestuffs is bound up, as is well known, with the exploitation of the coal-tar products. Faraday, Laurent, and Runge (1834) are prominent among those who isolated valuable hydrocarbons from tar, while Hofmann (1843-5) discovered aniline and its homologues therein. In 1856 Perkin obtained mauve (magenta) by the oxidation of aniline with chromic acid, and since then innumerable synthetic dyes have been produced, not only from coal-tar products (though these form the basis of the most widely-applied colours) but from other common aromatic substances as well. We should note especially the device, very soon introduced, of improving the solubility of a dye by increasing its acidity (sulphonation) or basicity (alkylation). The evolution of the various colouring matters can best be grasped by a chronological table :—

Mauveïne	Aniline (safranine)	—
Rosaniline	Triphenylmethane	Triamidotriphenyl carbinol
Quercetin	Flavone	—
Phosphine	Acridine	Amidophenylacridine
Methyl violet, etc.	Triphenylmethane	Alkylated rosanilines
Induline	Phenazine	—
Bismarck brown	Azo	Triamidoazo benzene
Rosolic acid	Triphenylmethane	Trioxytriphenyl carbinol
Martius' yellow	Nitro	Calcium dinitronaphtholate
Alizarin	Anthracene	Dioxyanthraquinone
Magdala red	Phenazine	(Safranine)
Resorufin	Phenoxazine	—
Fluorescein	Phthalein	Resorcinolphthalein
Eosin	,,	Tetrabromfluorescein
Chrysine	Flavone	—
Aurantia	Nitro	Ammonium hexanitrodiphenylamine
Pararosaniline	Triphenylmethane	Triamidotriphenylcarbinol
Lauth's violet	Phenthiazine	Diamidothiodiphenylamine
Methylene blue	,,	Tetramethyl- ,,
Chrysoidine	Azo	Diamidoazobenzene
Malachite green	Triphenylmethane	Diamidotriphenylcarbinol
Aurine	,,	Trioxytriphenylcarbinol
Biebrich scarlet	Azo	β-naphtholazosulphobenzeneazo-benzene sulphonic acid
Indigo	Indigo	
Congo yellow	Azo	From benzidine, phenol and sulphanilic acid
Indazine	Phenazine	—
Fisetin	Flavone	—
Rhodamine	Phthalein	Amidophenolphthaleins

1856 W. H. Perkin, sen.
1859 Verguin (from aniline and ortho- and para-toluidines).
1859 Rochleder (extraction from plants).
1862 Hofmann (fuchsine bye-product).
1867-75 Hofmann; E. and O. Fischer, etc.
1865 H. Caro and Dale.
1867 H. Caro and Griess.
1867 H. Caro and Wanklyn.
1868 Martius.
1869 Gräbe and Liebermann (synthetic).
1869 Hofmann.
1872 Weselsky.
1872 Baeyer.
1873 H. Caro.
1873 Piccard (natural sources).
1874 Gnehm.
1876 Rosenstiehl.
1876 Lauth.
1877 H. Caro.
1877 Hofmann.
1878 O. Fischer; Döbner.
1879 Dale and Schorlemmer.
1880 Nietzski.

Synthetic methods.

1880 Baeyer (from o-nitrophenylpropiolic acid).
1882 Baeyer and Drewson (from o-nitrobenzalacetone).
1890 Heumann (from anthranilic acid).
1889 Griess.
1891 O. Fischer and Hepp.
1897 A. G. Perkin (natural sources).
1898 Badische Anilin und Soda Fabrik.

If we now add another summary, showing the theoretical development of the formulæ of the various parent compounds concerned, it will be unnecessary to emphasize further the dependence of modern industry on the research laboratory :—

Class of Substance.	*Chief Investigations.*
Aniline and homologues	1834 Mitscherlich ($C_6H_5NO_2$) ; 1834 Runge ; 1841 Zin 1852 Béchamp ($C_6H_5NH_2$) ; 1845 Hofmann and M pratt (p-Toluidine)
Azo-bodies	Griess, 1859 (diazo reaction) ; 1862 (diazoamidobenzer 1866 (amidoazobenzene)
Indigo	Constitution by Baeyer and his students, 1865-1874
Alizarin	Constitution and subsequent synthesis by Graebe a Liebermann, 1868
Acridine	Constitution and synthesis by Graebe and H. Caro, 1
Triphenylmethane	Constitution and synthesis by Kekulé an l Franc mont, 1872
Phenazine	Constitution and synthesis by Claus, 1873
Phenthiazine (thiodiphenyl-amine)	Constitution and synthesis by Bernthsen, 1888
Phenoxazine	Constitution and synthesis by Bernthsen, 1887
Flavones and Xanthones	Constitution and synthesis by St. v. Kostanecki, A. Perkin, 1895-1905

§ 7. **Explosives**—Van Helmont, whose explanations of chemical processes have several times attracted attention by their clearness, ascribed the characteristic effect of exploding gunpowder to the production of much gas ; study of the evolved gases in this and other explosive reactions was not greatly engaged in, however, until the nineteenth century, during which their composition under varying conditions was made the subject of research by Debus, Bunsen, Abel, Nobel, and others. Berthelot's work on the thermo-chemistry of explosives is very important.

Of the individual members of this class gunpowder has of course been longest known, having been employed in fireworks by the Chinese and Moors. After its rediscovery by Schwarz in 1334 it came to be employed in warfare by the occidental

nations. It has remained practically the only explosive in which the oxygen necessary for combustion is supplied by means of an added substance (the nitre), unless we include a disastrous attempt of Berthollet's (1786) to substitute chlorate for nitre.

The more modern type, which consists usually of a carbon compound containing sufficient easily available oxygen for complete combustion, includes the fulminates, discovered by Howard (1800), characterized by Liebig and introduced as detonators by Ure (1831); the picrates, investigated by Fontaine, Designolles, and Abel; nitrocellulose (gun-cotton), discovered by Braconnot in 1823, and prepared by Schönbein in 1846 (Pélouze (1838) suggested its use in artillery, but much difficulty was found in manipulating it until in 1886 Vieille discovered the secret of detonating it safely); and nitroglycerine, first produced by Sobrero in 1847. The latter was first applied as dynamite (after absorption in kieselguhr) in 1862 by Nobel, Abel, Champion, and others, while mixed with gun-cotton it has been applied by these chemists and others, such as Vieille (1884), to the fabrication of smokeless powders (e.g. Nobel's mixture (1890) of gun-cotton, dynamite, and gelatine).

CHAPTER X

THE HISTORY OF PHYSICAL CHEMISTRY

We have to deal in this chapter with the direct application of physics to chemistry, and within the last thirty years so much progress has been made in this region that the bulk of the work which we shall chronicle will have been carried out during that period.

At the outset we should note that the basis of the whole science rests on two "laws"—the conservation of mass and the conservation of energy.

The first of these was proved by Lavoisier when he showed that in chemical reactions matter is never either created or destroyed, but quite recently (1893-1908) elaborate experiments have been carried out by H. Landolt in order to test how far the law is an accurate expression of fact, the final result being that it is rigidly correct to within the limits of one part in ten million.

The accompanying doctrine of the conservation of energy is due more to Mayer and to Joule (1842) than to any other physicists, though not a few workers dealt with the subject in the earlier part of the nineteenth century.

§ 1. **The Physical Chemistry of Gases**—The first to realize the varying chemical nature of different gases were van Helmont (who introduced the term "gas" about 1620) and Rey (who showed that air possessed weight in 1630). The relation of the volume of gases to external pressure was discovered by Boyle (1660) and Mariotte (1670), while the effect

of temperature was quantitatively investigated by Charles (1785) and Gay-Lussac (1808). Dalton (1807) showed that, in any mixture of gases, each exercised its own "partial pressure" independently of the rest. Again, in 1808, Gay-Lussac found that the volumes of reacting gases always bore a simple ratio to each other and to the volume of the products (if gaseous), and this served in certain cases to contradict Dalton's atomic hypothesis (cf. p. 33) until in 1811 Avogadro put forward the hypothesis that equal volumes of gases contained equal numbers of molecules (Ampère attempted to extend the same hypothesis to solids, with indifferent success, a few years later).

In the meantime, from a purely physical standpoint, others were developing the kinetic theory of gases. The idea that gas particles are in motion was expressed by Bernoulli (1738) and Herapath, but a physical estimation of their mean velocities was first made by Joule in 1851. The modern kinetic theory of gases was practically stated by Waterson (1845) in an unpublished paper which was only brought to light in 1892 by Lord Rayleigh, and consequently the fame of evolving the theory rests with Clausius (1857) and Maxwell (1860). From this in 1881 van der Waals constructed a modified form of the "gas-equation" $PV = RT$ (Horstmann), which should express the deviations from Boyle's and Gay-Lussac's laws shown by readily liquefiable gases, and also to a smaller extent (Amagat, 1880) by the then-called permanent gases (nitrogen, hydrogen, oxygen). This equation,

$$\left(p + \frac{a}{v^2}\right)(v - b) = RT \text{ (where } a \text{ and } b \text{ are specific constants)},$$

is so accurate an expression of fact that by its means, on the one hand, Guye and Friedrich were able in 1900 to deduce practically coincident values for the "gas-constant" R from measurements of different gases, and, on the other, Daniel Berthelot (1899) has theoretically calculated the atomic weights of

various elements from the densities of their compounds (or of the elements themselves) determined by Regnault (1845), Lord Rayleigh (1888), and others. The values so obtained agreed excellently with those from chemical data.

The *liquefaction of gases* was a subject of careful study by Northmore (1805), who liquefied chlorine, and by Michael Faraday (1823), who condensed ammonia, sulphur dioxide, and other gases by the combined application of considerable pressure and a freezing mixture. His principle was improved by later workers, such as R. Pictet (1877), Cailletet (1877), Wroblewski and Olzscewski (1883), and, finally, Dewar (1884), by increasing the pressure and the degree of cold, so that all the known gases (even the so-called permanent ones), with the exception of hydrogen and helium (discovered later), had been liquefied by 1885. Dewar succeeded in liquefying hydrogen in 1898, and in the meantime a new principle (Hampson-Linde, 1895, the intense cooling of a gas by its own expansion when already cooled under great pressure) led to the cheapening of liquefaction processes. Finally, H. Kammerlingh Onnes condensed helium in 1908 to a colourless liquid boiling at 4·5° Abs., and has also obtained it in the solid state.

In 1821 Cagniard de la Tour noticed that many gases could not be liquefied above a certain temperature by any pressure, and in 1869 Andrews minutely studied the phenomenon and found that for each gas there existed a temperature above which no amount of pressure would condense it; he called this the *critical temperature* and the pressure necessary to produce liquefaction at that temperature the *critical pressure*, while the specific volume of the liquid formed was the *critical volume*. Much important theoretical work has since been carried out on the critical data, notably by Mendelejew (1884) and by Ramsay and Young (1894).

Finally the decomposition of some gases by heat and their reformation on cooling was studied by Deville in 1857 and named "*dissociation*". About the same time Kopp and Kekulé

observed the effect and set it down to partial decomposition. Gaseous dissociation has been studied quantitatively by methods of effusion (sal ammoniac, Pebal, 1862), colorimetry (phosphorus pentachloride, Deville; nitric peroxide, Salet, 1868), and specific heat (nitrogen peroxide, acetic acid vapour, Berthelot and Ogier, 1882).

§ 2. **Crystallography**—This sub-science, so important for mineralogy, was given a definite shape by Romé de L'Isle, Häuy, and Werner, who in the early years of the nineteenth century classified crystals according to physical form and assumed that difference in form entailed difference in chemical composition. This was overthrown later by Mitscherlich's discovery of polymorphism (1821). Later crystal-systems, by means of which all crystal-forms were finally divided into thirty-two geometrical classes, are due to Hessel (1830), Gadolin (1867) and P. Curie (1884).

In 1888 Reinitzer noticed that cholesteryl benzoate, before melting to a clear liquid, passed through a turbid or milky phase, and in 1890 other instances were observed by Gattermann. Lehmann (1890) found that the turbid liquid rotates the plane of polarized light, and must therefore be doubly-refracting and possess crystalline structure. Such substances are said to be *liquid crystals*, and although Tammann (1901) disputed the crystalline structure, the previous explanation is usually adopted at the present time.

The *relation of crystalline form to chemical composition* has naturally been the subject of much study. In 1846 Buys-Ballot stated that the elements and simpler compounds tended to crystallize in the simplest forms (regular and hexagonal) and more recently Retgers has statistically demonstrated the truth of the proposition (1892). Before this, however, Mitscherlich discovered *isomorphism* (1819), following on Gay-Lussac's and Bendant's observations on the growth of potash alum in ammonia alum, and of ferrous sulphate in copper sulphate solutions respectively. Mitscherlich based his views of isomorphism on

phosphoric and arsenic acid salts, selenic and sulphuric acid salts, and the alums and oxides of iron, chromium, and aluminium, and, with Berzelius, held that isomorphous bodies contained similar atomic structures—a point utilized by Berzelius to assist in determining atomic weights. Fuchs, similarly, discussed the constitution of isomorphous minerals (1872).

Finally, reference must be made to Mitscherlich's further discoveries of *dimorphism* and *polymorphism* (1821), and to Scherer's use of the term *polymeric isomorphism* (when atoms had been replaced by an atomic group to form an isomorph). Kopp's work on the specific volumes of isomorphs is noteworthy.

Other interesting points are the phenomenon of *isogonism* or *hemihedry* observed by Pasteur in 1861, wherein the slightest change of constitution (change of asymmetric configuration) causes a similar change in the position of the crystal facets, and that of *morphotropy*, studied by Groth (1876)—the definite alteration of form caused by definite substituents in organic compounds, especially in the aromatic series.

In conclusion, we have to describe the comprehensive theory recently elaborated by Barlow and Pope (1906), who "regard the whole of the volume occupied by a crystalline structure as partitioned out into polyhedra, which lie packed together in such a manner as to fill the whole of that volume without interstices. The polyhedra . . . are termed the spheres of atomic influence of the constituent atoms." The crystalline forms of many of the elements and simpler compounds, at all events, agree with the postulates of this theory, which is also capable of furnishing a steric formula for benzene expressing, according to the authors, all the necessary chemical facts (cf. chap. vi. p. 99).

§ 3. **Solutions**—The study of mechanism of solutions has almost always been developed from an electrolytic point of view, and therefore we may pass over the earlier history of this branch by referring to the theories of electrolysis dealt with in chap. iv.,

§ 4. We are thus left with the discussion of the *osmotic pressure* of solutions, a field opened up by the work of Pfeffer (1877) who made use of Traube's "semi-permeable membranes" (1867). Pfeffer found that substances in solutions obeyed definite laws with reference to their osmotic pressure, etc., but it was van 't Hoff who first perceived that dilute solutions are amenable to the same laws as gases, and that hence, among other corollaries, it follows that the molecular weight of a dissolved substance is related to the vapour pressure of the solution. This led to the determination of molecular weights by lowering the vapour pressure of a solvent (Raoult, 1887) or, what amounts to the same, lowering of freezing-point or elevation of boiling-point; it then appeared that solutions of electrolytes in water gave abnormal values for the molecular weight, and this found an explanation in Arrhenius' ionic theory (1886), which assumed that ions exist ready formed in dilute solution, the electric current exerting simply a directive effect. This does not, however, afford an absolutely perfect explanation, and it seems likely that the final theory of solutions will be a combination of Mendelejew and Arrhenius' theory of hydration of ions and molecules (1888) for concentrated solutions, with the ionic theory for dilute solutions and electrolysis.

The *electrical conductivity* of solutions has been the subject of experiment ever since Hittorf (1853-9) determined the "transport numbers" for the migration of the ions and Kohlrausch (1879) discovered, first, the relation of the "transport number" to conductivity (1879) and then the law of the "independent migration of the ions" (1885), whereby the total conductivity of a solution was shown to depend upon the sum of the two ionic velocities. The *conductivity of acids* (organic, Ostwald, 1878-87; Walden, 1891; very weak acids, Walker, 1900) has been shown to be a measure of their "relative affinity," as already described (chap. iv. p. 57), while that of *pure water* has been concordantly determined by the E.M.F. of an acid-alkali cell (Ostwald, 1893), the hydrolysis of salts (Arrhenius,

1893), and the rate of hydrolysis of methyl acetate in pure water (van 't Hoff and Wiis, 1893), and finally, by direct measurement (Kohlrausch and Heydwiller, 1894).

Amphoteric electrolytes (both acidic and basic, such as methyl orange, sulphanilic acid, glycocoll, zinc hydroxide and other feebly acidic metal oxides) have been studied by Küster (1892), Winkelblech (1901), J. Walker (1904), and many others; similar fields have been opened by Hantzsch in the case of *pseudo-acids and bases* (1896, cf. p. 104), and Noyes and Whitney on *complex ions* ("double salts") in 1894.

Conductivity in solvents other than water has been investigated by Tessorin (1896, formic acid), Carrara (1896, acetone) and especially by Jones (1902-6) and by Walden (1901-6, tetra ethylammonium iodide in liquid sulphur dioxide, sulphur oxychloride, ether, etc. etc.), while Kahlenberg (1902-3) has proved that the dissociating power of a solvent depends directly upon the magnitude of its dielectric constant.

Finally, Nernst has recently given theoretical explanations of "Volta's pile" and of the ordinary galvanic cells by means of a diffusion theory based upon van 't Hoff's theory of solutions.

The solutes we have so far dealt with are all crystalline substances, but we must now refer to another branch of soluble bodies, the *colloidal* substances. The purification of these has been rendered possible by the process of *dialysis*, discovered by Graham in his researches on *diffusion*.

The phenomenon of diffusion seems to have been first noticed by Parrot in 1815, and a mathematical treatment of the subject appeared by Ficks in 1855. In the meantime the different rates of diffusion and effusion of gases had been studied by Graham in 1851, and later the same chemist extended his observations to the diffusion of dissolved bodies through animal membranes. He found that these were permeable to one set of substances (crystalloids) and impermeable to others such as dextrin, silicic acid, tannin, which he termed *colloids* (1862). Work on osmosis by Jolly, Brücke, and Pfeffer (1877) proved

that the osmotic pressure of such bodies was very small, and consequently their molecular weight should be enormously large, that of many being greater than 10,000 (Linebarger found by osmotic pressure measurements in 1892 that tungstic acid, one of the simpler colloids, possessed a molecular weight of 1700-1720; $(H_2WO_4)_7 = 1750$). Much work has been done of late years on this subject (especially by Bredig, 1903, and Billitzer, 1903), but the structure of colloids remains very uncertain indeed and we will therefore simply recall Sabarejew's division of colloids (1891) into those of molecular weight greater than 30,000 (starch, silicic acid, iron hydroxide, etc.), and less than 30,000 (dextrin, tannin, molybdic acid, etc.).

§ 4. **Molecular Weight Determination**—It may be useful to give a summary of the physical methods lately developed for its estimation of molecular weight; these depend mainly on determination of *vapour density* or of *osmotic pressure* (direct or indirect).

(*a*) *Vapour Density Methods.*—The theory of these methods depends of course mainly upon the application of Avogadro's hypothesis; it must be remembered, however, that, while in former times the approximate determination of vapour density was made to serve as a check on the multiple of the chemically-determined equivalent which was to be accepted as the true atomic or molecular weight (Cannizzaro, 1858), more recently the application of van der Waal's equation (D. Berthelot, 1899) has led to exact determinations of molecular weight by gas density in numerous instances.

Four different principles have been utilized in succession for the experimental determination of vapour density:—

Measurement of the weight of a given volume of an already gaseous substance (Regnault, 1845; Lord Rayleigh, 1888-; Leduc, 1892-8; Morley, 1895).

Measurement of the weight of a given volume of vapour (Dumas, 1827; applied by Dumas and by Mitscherlich to the elements sulphur, arsenic, phosphorus and mercury).

Measurement of the volume of a given weight [Hofmann, 1868, designed an improved form of Gay-Lussac's apparatus (1801), which was further modified for high temperature work by Ramsay and Young (1885)].

Measurement of the volume of air (at atmospheric temperature and pressure) displaced by the vapour from a given weight of substance (Victor Meyer, 1878). This has been found to be most generally applicable, especially for very high temperatures (up to 1900° C., Biltz, 1896; 1700° C., Nilson and Pettersen, 1889). By this means the atomic weights of silicon, beryllium, thorium and germanium, amongst others, have been established from the vapour densities of their chlorides, while the dissociation of compounds like aluminium chloride (Al_2Cl_6) and stannous chloride (Sn_2Cl_4) into simpler molecules has also been studied (V. Meyer, Nilson and Pettersen).

(*b*) *Osmotic Pressure Methods.*—The discovery of the connexion between osmotic pressure and molecular weight was recorded in the last paragraph, and some account will now be given of the practical application of the principle. Guldberg (1870) and van 't Hoff (1886) independently deduced from the laws of vapour pressure that the depression of freezing-point and elevation of boiling-point were both proportional to alterations of vapour pressure, and it appeared later that both depend on the osmotic pressure, and hence, on the molecular weight of the solute. This led to four new methods of molecular weight estimation :—

(i) *Direct Measurement of Osmotic Pressure of Solutions.*—This is chiefly of theoretical interest, since it is difficult to obtain a great degree of accuracy. Pfeffer (1877) used semi-permeable membranes of cupric ferrocyanide, Tammann (1888) utilized drops of potassium ferro-cyanide in copper sulphate solution, and de Vries (1888) taught how to prepare isotonic solutions by observation of the behaviour of certain plant-cells therein (plasmolysis), and obtained in this way a good determination of the molecular weight of raffinose ($C_{18}H_{32}O_{16}$).

The Earl of Berkeley and Hartley (1906) have recently made important additions to the knowledge of osmotic pressure.

(ii) *Indirect Measurement of Osmotic Pressure of Solutions.*—

1. Lowering of vapour-pressure of solvent (Raoult, 1887; also difficult to manipulate with sufficient accuracy).

2. Depression of freezing-point of solvent. Blagden (1788) and Rüdorff (1861) noticed that the depression was proportional to the amount of dissolved substance; Coppet (1871) and Raoult (1882) saw that molecular amounts of different solutes depressed the freezing-points of a given solvent to the same extent; Beckmann (1888) devised a convenient form of apparatus with a specially delicate thermometer, in both of which sundry alterations have been made by later workers; and Vernet and Abegg (1894) further developed the mathematical theory of the process.

3. Elevation of boiling-point of solvent (Beckmann, 1889). The last two methods have found a great sphere of utility.

§ 5. **Relation of Physical Properties to Chemical Constitution**: (*a*) **Mechanical**—Here we have to deal once more with a problem whose general importance has only been realized within the last twenty or thirty years, namely, the dependence of the physical properties upon the constitution of compounds. It is now, however, generally admitted that this is a subject of extreme importance to the development of theoretical chemistry. A definite systematization of such properties was not known until Ostwald in 1891 defined them as *additive*, depending simply on the atomic composition of the molecule—*mass* is the only perfect example—*constitutive* (influenced by the mode of union of the atoms—*optical activity* and *absorption spectra* are perhaps the most striking instances) and *colligative* (depending on the number of molecules—*vapour density*, *osmotic pressure*, etc.).

We shall now proceed to give a very brief and necessarily incomplete résumé of the development of the present views on different types of properties, and will commence with those

which, for want of a better name, may be called mechanical properties.

(*a*) *Specific Gravity; Specific and Molecular Volume.*—The methods devised by physicists for measuring the density of gases have already been summarized; the specific gravity of liquids used to be generally measured by the specific gravity bottle, but more refined methods have been introduced by Sprengel and Ostwald (1873, the pycnometer), and by Kohlrausch and Hollwachs (1894, the areometric method, based on Archimedes' principle). The density of solids is not so easy to obtain with perfect accuracy, but the principles chiefly used have been that due originally to Archimedes, and that whereby the solid is made to swim free in a liquid mixture, whose composition is suitably adjusted by means of a heavy component (e.g. methylene iodide) and a light component (e.g. benzene). This device was brought to a high degree of perfection by Retgers in 1889.

The specific volumes of elements and compounds were first systematically studied by Kopp (1842-1855), who claimed that it was a purely additive function. Later work by Schröder (1880), Lossen (1882), Horstmann (1886-8), and others, notably Traube, has shown that although Kopp's view is roughly correct, definite modifications are introduced by constitutional influences. Researches on the specific gravity of liquid mixtures (Linebarger, 1896) have also proved interesting, since in many cases evidences of "association" or loose molecular combination have been found.

(*b*) *Surface Tension.*—The phenomena of capillarity were explained by Young in 1804, and attention has frequently been paid to the property since, its measurement having been effected by Laplace, Gay-Lussac, J. Traube (1891), van der Waals (1894), and others. The temperature coefficient $\frac{d(\gamma s)}{dt}$ has been shown to be constant for nearly related members of the same homologous series and its utility as a means of testing the

molecular complexity of liquids has been proved by Eötvös (1886), and by Ramsay and Shields (1893).

(*c*) *Internal Friction.*—The viscosity of gases has been chiefly studied, from a physico-chemical standpoint, by L. Meyer (1879), and Staedel (1882), while much work has been done with respect to solutions by Ostwald (1891), who designed a convenient viscometer, and to liquids by Thorpe and Rodger (1894-6), and to liquid mixtures of many types by Dunstan (1904 onwards) and his students, and in lesser degree by numerous other workers. The fact that molecular association can take place in solid as well as in liquid mixtures has been shown by Trouton and Dunstan (1908) in the case of certain alloys, the method used being the stretching of a wire of the substance in question by a given weight.

(*d*) *Melting-point.*—Attempts have from time to time been made to give quantitative rules for melting- and boiling-points, but with very little success. The most notable regularities are that the property is affected very little by pressure (Kelvin, 1850); that several series of organic acids are characterized by the melting-points of the odd members of the series lying on one curve, while those of the even members are on another (Baeyer, 1877); that in aromatic compounds, nitro-substituents melt higher than bromo-derivatives, and these, again, higher than the corresponding chloro-bodies (Petersen, 1874), and a para-substituted compound melts in general higher than either the meta- or ortho-derivative (Beilstein, 1886).

The only accurate methods of melting-point determination are the immersion of a delicate thermometer in a large amount of the heated solid, or of the super-cooled liquid (Landolt, 1888).

(*e*) *Boiling-point.*—Kopp sought to show that equal differences in constitution produce equal differences in boiling-point (1845), but soon found that this was a very limited rule. Regularities have been found also by Tollens (1869), Marckwald (1888), Henry (1888), Earp (1893), and others; the general result being :—

(i) Increase of molecular weight tends to increase the boiling-point.

(ii) In organic isomers, the normal compound has the highest, and the most compactly arranged molecule the lowest boiling-point.

(iii) A substituent in a central position in the molecule tends to volatility.

In 1891 Vernon suggested that many irregularities were due to polymerization and from the behaviour of different series estimated the degree of polymerization of water, sulphuric acid, sulphur, and other substances from their boiling-points. The relation between boiling-point and critical temperature was made clear by Thorpe and Rücker (1884).

§ 6. **Relation of Physical Properties to Chemical Constitution** : (*b*) **Electrical**—We have already discussed the most important electrical property (conductivity) in connexion with the history of electrolysis (pp. 56 ff.), and we only need refer here to the study of *magnetism* and of *di-electric constant.* The former has been studied by Plücker (1857) and by Henrichsen (1888) who found that all the organic compounds he examined were diamagnetic and that the property was mainly additive, although the ethylenic linking, — C : C —, exerted abnormal influence. Jäger and St. Meyer (1897) examined the magnetism of elements in compounds, more particularly those of chromium, iron, and manganese.

Measurements of *di-electric constant* have been carried out by Silow (1875) by the electrometer, by Nernst (1893) by the condenser method, and by Drude (1897) by means of stationary electric waves. The latter physicist and Walden (1906) have carried out extensive work on the di-electric constants of many organic compounds. Kahlenberg (1903) showed that the dissociating power of a solvent upon electrolytes was connected with the dielectric constant.

Thermal properties (specific heat, etc.) will be considered in § 9 of this chapter.

§ 7. **Relation of Physical Properties to Chemical Constitution** : (*c*) **Optical**—The history of *optical activity* having already received attention (p. 111), we will pass on to that of—

(*a*) *Refractive Power*.—The property of refraction of light, known to physicists for a very long time, has more recently been found to be one of the most useful physical guides to chemical constitution. The earlier workers from a chemical standpoint include Cahours and Deville; the first formula for molecular refractive power $\left(\frac{M}{d}(n-1)\right)$ was put forward by Gladstone and Dale in 1858 (Landolt, 1864); a second and more correct expression $\left(\frac{M}{d} \cdot \frac{n^2-1}{n^2+2}\right)$ was deduced theoretically and confirmed practically by Lorenz and Lorentz in 1880. Since 1880 the most prominent, but by no means the only, worker in the field has been Brühl, who has shown that the property is sufficiently additive to admit of calculation, since the constitutive influences are so regular that numerical values may in general be assigned to them. When, however, two unsaturated groups occur side by side in the molecule anomalous refractivities are observed, and this is accounted for by Brühl as being due to the "conjugation" of two groups rich in residual affinity. Brühl has also been a notable worker in connexion with *molecular dispersion* of light, a property found to be more constitutive than refractive power.

(*b*) *Magnetic Rotation*.—In 1846 Faraday discovered that any transparent substance in a magnetic field deflects the plane of vibration of polarized light. This property has been very thoroughly studied by Sir W. H. Perkin, who defined specific and molecular magnetic rotatory power, and found the property to be mainly additive, but in a small degree constitutive, and showing anomalous values in the case of conjugated unsaturated systems. There have been few other prominent workers in

this section, but we may refer to Jahn's study of the additive properties of the magnetic rotatory powers of ions (1891).

(*c*) *Spectroscopy*.—As long ago as the middle of the eighteenth century the distinction of sodium from potassium salts by means of their flame-colorations was known to Marggraf and to Scheele, but more systematic examination of the spectrum was entered upon by Wollaston (1802), Herschel (1822), and others. The spectra of coloured flames were also studied by Miller (1845), Swan (1856), and others, but it was not till 1859 that Kirchhoff and Bunsen established the law that each chemical element has its own characteristic spectrum. From that time the discovery of new elements by the spectroscope has been effected by Bunsen, Crookes, Lockyer, Ramsay, and others, while various types of *emission* spectra (spark, arc, and phosphorescent) have been pressed into service. In 1863 Roscoe and Clifton discussed the alteration of the spectrum of a substance by varying physical conditions and by change of constitution. On the other hand, mathematical relations of the spectral lines were sought for by Stoney (1871), Maxwell (1875), Lecoq de Boisbaudran (1889), and Rowland (1893-), and the regular formation of some elementary spectra began to appear evident. In 1885 Balmer produced a formula by which to calculate the hydrogen spectrum, and in 1891 Kayser and Runge gave similar expressions, but not quite so successfully, for some of the metals. Twelve years later Riecke suggested an analogy between the lines of a spectrum and the harmonic vibrations of sound, and in 1906 Stark by an extension of the idea conceived the lines as the expression of electronic vibration and deduced various electronic "atomic" formulæ therefrom. Such, briefly, is the development of our knowledge of the constitution of spectra—a line of research which by co-ordinating optical properties with the electronic theory of matter may possibly in course of time furnish an explanation of the interdependence of physical properties and chemical constitution.

Another equally fruitful field has been found in *absorption*

spectra. Wollaston (1802) and Fraunhofer (1814) noticed the first case of this in examining the solar spectrum, and with their work as basis, astronomy has been able to determine the qualitative composition of many of the stars and planets.

The absorption spectra of solutions of electrolytes and of organic compounds have engaged numerous chemists, of whom we have only space to mention a few. Ostwald and others have shown that in dilute solutions each ion has its own definite spectrum. The work on organic compounds concerns more particularly the ultra-violet, invisible part of the spectrum, and has been carried out by Krüss (1883-8), Vogel (1891), Hartley and Dobbie (1899), Baly and co-workers (1905), and many others. Most of the research has been done in endeavours to follow constitutional change by means of the property.

An interesting practical application is that made by Witt (1876), Nietzski (1879), and others, who have based theories of colouring and dyeing upon their observations. Witt introduced the conception of chromophores or colour-producing groups and chromogens or groups which must be attached to a chromophore before the characteristic colour is exhibited. Schütze (1892) traced a connexion between colour and increasing molecular weight.

(*d*) *Fluorescence* has been found to be almost as constitutive a property as absorption spectra or optical activity. Notable names in connexion with this property are R. Meyer (1897), Kauffmann, and Kehrmann. Kauffmann applied to fluorescence a similar explanation (of "fluorophores" and "fluorogens") to that of colour given by Witt, and, further, has found a relation between the property and the disposition of "partial valencies," while Hewitt (1900) has observed that in very many cases fluorescence is accompanied by a possibility of "double symmetrical" tautomerism in the molecule, and suggests that the phenomenon is connected with molecular vibration due to such dynamic isomerism.

§ 8. **Photo-chemistry**—The chemical action of the ultra-

violet rays of light is important both in its connexion with modern theory and in its practical applications in the direction of photography, etc. Dealing with the latter aspect first, it would seem as though the darkening of silver salts was known to Boyle (who set it down to atmospheric influences), while Schultze a few years later declared the effect to be produced by light. Scheele examined the effect of the solar spectrum in detail and found the action to be concentrated in the violet part, and, finally, Ritter in 1801 ascribed it to the ultra-violet rays. The development of photography, after its initiation by Daguerre and Talbot in 1839, was especially furthered by Nièpce (collodion films, 1847), Bennett (bromo-gelatine films, 1878), and Lippmann (colour photography, 1892).

In the meantime other actinic chemical reactions were brought to light, especially by Davy and Faraday (union of CO and Cl_2; H_2 and Cl_2; chlorination of marsh-gas, etc.), and a detailed study of the mechanism of the process was made by Bunsen and Roscoe (1857). Their results showed that such actions were supported by certain light-waves in the ultra-violet region, which in this way supplied the necessary energy for the change. That energy was given up by the waves in question followed from the fact that a given stream of the rays lost all capacity for chemical action after passing through, for example, a mixture of hydrogen and chlorine (*photo-chemical extinction*).

It was also noticed that the action of light usually commenced very sluggishly and then rose to a maximum (*photo-chemical induction*); this was explained subsequently on the hypothesis that an intermediate product was first formed which was itself responsible for the final more rapid rate of change. (Burgess and Chapman, 1904, and Wildemann, 1902.) A similar principle to this (the "*latent action*" of light) forms the basis of the developing process, which has been explained as being set up by the particles of metallic silver or of silver sub-halide (Luther, 1899) produced in the first momentary ex-

posure. Subsequent improvements in developing, toning, fixing, etc., have followed as new organic reagents suitable to these purposes have been synthesized.

Other more recent examples of actinic action are the decomposition of various acids (succinic, tartaric, etc.) by sunlight into carbon dioxide and simpler acids in presence of uranium oxide (see Kamp, 1893), and the synthesis of indigo from an ethereal solution of benzal-*o*-nitroacetophenone in sunlight (Engler and Dorant, 1895).

§ 9. **Thermo-chemistry**—We have to deal here mainly with the relations to chemistry of specific heat, latent heat, and heat of reaction.

(*a*) *Specific Heat of Gases.*—Measurements of the specific heat of a gas at constant pressure were made by Delaroche in 1811, but more accurately by Regnault (1853) and Wiedemann (1876). Regnault's method is the most important for the value at constant volume. The difference in the values ($C_p - C_v = 1{\cdot}99$) has been used by physicists (e.g. Mayer, 1842) to determine the mechanical equivalent of heat, but to chemists the ratio $C_p : C_v$ is more interesting, since this has been proved to furnish an indication of the molecular complexity of the gas in question. Methods for the direct measurement of the ratio are due to Clément and Desormes (adiabatic expansion, 1815) and to Kundt and Warburg (ratio of sound wave-lengths in the experimental and in a known gas, 1876). The most famous applications of this formula are for the monatomic gases mercury (vapour), and helium, argon, and their congeners. Measurements of the specific heat of gases at high temperatures show that their heat-capacity remains constant up to 2700° C. (Le Chatelier, 1881; Berthelot and Vieille, 1884).

(*b*) *Specific Heat of Elements and Compounds.*—In 1818, Dulong and Petit proved, though not very accurately, that "the capacity for heat of many atoms is the same," namely,

$$\text{spec. heat} \times \text{atomic weight} = 6{\cdot}3;$$

this rule was seized upon by Berzelius as a method of

checking atomic weights—a sphere in which it has proved exceedingly useful, although at first more credence was given to deductions from isomorphism than from specific-atomic heat. Neumann educed a similar rule for compounds in 1831, and a possibility of removing some of the discrepancies of the Dulong-Petit law appeared when Regnault (1840), Kopp (1864) and others showed that specific heat in many cases varied markedly with temperature. Remeasurement of anomalous values such as those for boron, beryllium, silicon and carbon, over an extended upward range of temperature has, in the hands of Weber (1875), Nilsen and Pettersen (1880), and Tilden (1905), led to the verification, within narrow limits, of the Dulong-Petit law.

We must also mention work on the specific heat of liquids and liquid mixtures, undertaken with a view to finding structural influences; this has, however, not received so much attention as in the case of some other properties.

(*c*) *Latent Heat.*—The property of latent heat has been less directly connected with chemical work than specific heat, but we may recall that it was discovered by Joseph Black in 1762 and that Lavoisier more thoroughly investigated it. The determinations of freezing-point by the method of supercooling and in Beckmann's depression of freezing-point apparatus are of course founded on the development of latent heat in solidification.

(*d*) *Heat of Chemical Combination.*—Employing calorimetric methods which nowadays appear somewhat crude, Lavoisier and Laplace, and also Davy, concluded that the same amount of heat is evolved in decomposing a compound as is absorbed in synthesizing it, or conversely, according to whether the compound is *endo-* or *exo-thermic* (a term introduced by Berthelot, 1865). In 1840 Hess put forward what are known as his "Laws of constant heat summation," stating that the heat of formation or reaction of a given chemical system is always the same, and thus anticipating the deductions made from the

principle of the conservation of energy (mechanical equivalent of heat), stated a few years later by Joule.

Favre and Silbermann (1853) introduced improvements in the calorimetric measurements, and Andrews, Graham, and Marignac are notable amongst those who studied thermo-chemistry after Hess' time. The most far-reaching work, however, has been carried out by Julius Thomsen (since 1853) and by Berthelot (since 1865).

Especially noteworthy are their observations that the heat of neutralization of any strong acid by any strong base in dilute solution is constant (a fact made clear later by the ionic dissociation theory, the essential reaction being in all cases $\overset{+}{H} + \overset{-}{OH} = H_2O$ + 13700 calories), and their attempts to throw light upon the constitution of benzene from thermo-chemical data.

§ 10. **Electro-chemistry**—We may refer to chap. iii. § 7 for the history of the electronic theory, and the various theories of electrolysis, to § 3 of the present chapter for further reference to the conductivity of solutions and the theoretical problems connected with galvanic cells, and to chap. ix. § 3 for the application of electricity to metallurgy and technical chemistry in general.

It may be remarked here, however, that the mathematical treatment of the processes of galvanic current production was commenced by Lord Kelvin (Sir W. Thomson) and worked out by Helmholtz, van 't Hoff, Nernst (1889) and others, who have applied it, not only to the simple concentration-cell, but to the more complex elements of the common forms of galvanic cells and to accumulators.

Of recent years electrolytic oxidation and reduction has received much attention in view of the possibility of preparing technically valuable organic substances thereby. Haber (1898) has shown that the reduction of nitro-benzene can be carried to practically any definite degree from azoxybenzene down to aniline by regulation of the cathode potential, while, corre-

spondingly, Davy-Hénault (1900) found that, according to the potential at the anode, aldehyde, or acetic acid, or higher products could be more or less quantitatively obtained by the oxidation of alcohol.

In conclusion, a summary of the theoretically interesting electro-syntheses of the simpler organic compounds may be useful :—

Acetylene, methane, etc. ; Berthelot, 1868.
Hydrocyanic acid (from acetylene and nitrogen, as well as from cyanogen and hydrogen) ; Berthelot, 1868.
Paraffins from fatty acids ; Kolbe, 1849.
Olefines and acetylenes from saturated and ethylenic diabasic acids (respectively) ; Kekulé, 1864.
Succinic ester, from potassium ethyl malonate ; Crum Brown and J. Walker, 1891.
Ethane tetracarboxylic ester, from disodium ethyl malonate ; Mulliken, 1895.
Keten from acetic anhydride ; Wilsmore and Stewart, 1907.

§ 11. **Chemical Statics and Dynamics**—We have seen (chap. iv. § 1) how the evolution of Wenzel's and Berthollet's views on chemical affinity led to Guldberg and Waage's statement of the law of mass action. Since their time, many reactions have been tested with reference to the characteristic equation

$$V = KC_1C_2\ldots - K^1C_1^1C_2^1\ldots$$

with the result that chemical actions have become susceptible to mathematical treatment.

We will indicate the chief instances which have led to this state of affairs, taking first of all the case in which the reaction reaches a state of equilibrium, represented by the equation

$$C_1C_2\ldots = KC_1^1C_2^1\ldots \text{ (\textit{chemical statics})}.$$

The following examples have served to point out the truth of this law :—

The reaction $H_2 + I_2 \rightleftharpoons 2HI$	Hautefeuille, 1867; Lemoine, 1877.
The dissociation $N_2O_4 \rightleftharpoons 2NO_2$	Natanson, 1885.
*The dissociation $S_8 \rightleftharpoons S_2$	Biltz, 1888-1902.
The reaction $CaCO_3 \rightleftharpoons CO_2 + CaO$	Le Chatelier, 1888.
The reaction $2CO_2 \rightleftharpoons 2CO + O_2$	Le Chatelier, 1888.
Ester-formation from acid and alcohol	Berthelot and Péan de St. Gilles, 1863.
Mutual solubility of liquids	Berthelot and Jungfleisch, 1872.
Distribution of a substance between two solvents	Nernst, 1891. Hendrixson, 1897.

The methods used varied with the nature of the reaction and embraced both chemical and physical determinations.

The distribution of a base between two acids, or *vice versa*, has also been studied from this standpoint by Julius Thomsen (thermo-chemically, 1854), Ostwald (dilatometrically and by change of refractive power, 1878), Jellet (optical activity, 1875), and Lellman and Schlesmann (absorption spectra, 1892).

On the other hand, the study of the rate of chemical change by means of the law of mass-action (chemical kinetics) has resulted in the classification of reactions according to the number of molecules taking part, each class possessing a characteristic reaction constant. The first instance of this was the inversion of cane-sugar, studied polarimetrically by Wilhelmy in 1850, and more recently by Ostwald and Arrhenius. Ostwald (1883) has examined many other cases of salt or ester hydrolysis and his work has been supplemented by that of Walker (1889) and Löwenherz (1894) who showed that the rate of ester hydrolysis was affected by the acid, but not by the alcohol, set free in the reaction. All of this tended to the view that the determining factor of the hydrolysis was the hydrogen ion, an idea further supported by the fact that all such reactions appeared as bi-molecular changes.

* It has been proved incidentally that the only two forms of sulphur vapour are S_2 and S_8, others, such as S_6, S_4, being simply mixtures of these two.

We will give here a few instances of the various types of reaction studied in this way, the majority being uni- or bi-molecular: a large number were collected by van 't Hoff ("Etudes de dynamique chemique," 1884):—

Unimolecular—

Potassium permanganate and oxalic acid (in large excess)—Harcourt and Esson, 1865.

Decomposition of dibromsuccinic acid—Van 't Hoff, 1884.

Decomposition of radium emanation—Mme. Curie, 1904.

Bimolecular—

Inversion of cane-sugar—Wilhelmy, 1850.

$R \cdot COOEt + NaOH$ (action of $O\bar{H}$ ion)—Van 't Hoff, 1884; Ostwald, 1887.

$CH_2Cl \cdot COONa + NaOH = CH_2(OH)COONa + NaCl$—Van 't Hoff, 1884.

$C_2H_5I + AgNO_3$—Chiminello, 1896.

Decomposition of polybasic acids—Knoblauch, 1898.

Termolecular—

$2FeCl_3 + SnCl_2 = SnCl_4 + 2FeCl_2$—Noyes, 1895.

Quadrimolecular—

$HBrO_3 + HBr$
$2\overset{+}{H} + \bar{B}r + \bar{B}rO_3 = HBrO + HBrO_2)$ } J. W. Walker and W. Judson, 1898.

Quinquemolecular—

$2KI + 2K_3Fe(CN)_6$
$2\bar{F}e(\bar{C}\bar{N})_6 + 3I^- = 2\ \bar{F}e(\bar{C}\bar{N})_6 + I_3$ } Donnan and Le Rossignol, 1903.

We have said that hydrolysis has been shown to be effected by the "catalytic" action of ions, but *catalysis* is a term which, although of long standing, does not mean much.

Many instances of chemical change which, if not altogether suspended, were very slack in the absence of a definite assisting substance, became known during last century. Such additional substances, which passed through the reaction apparently unchanged, were called catalysts.

Interesting additions to the knowledge of this subject were made when Dixon and Baker (1884-6) showed that many common reactions (union of hydrogen and oxygen; hydrogen

and chlorine ; ammonia and hydrochloric acid, etc.) did not take place in the perfect absence of moisture, when Bigelow observed a kind of inverse catalysis in that many organic substances retarded the oxidation of sodium sulphite by oxygen (1898) and when Hjelt (1891) and Henry (1892) observed cases of "auto-catalysis" (the rate of decomposition of substances increasing abnormally in consequence of one of the products of decomposition acting as catalyst). Catalysis is at present usually defined as the alteration of the rate of chemical reaction by the presence of an independent substance.

§ 12. **The Phase Rule**—The manner in which the components of a physical system can co-exist, and the transformations which such a system will undergo as the number of its components, or their physical state, or extraneous conditions, are altered, were summed up by Gibbs (1874-8), and expressed by a simple equation which has been called the "phase rule". In accordance with the rule numerous diagrams of different systems have been constructed, by means of which the composition of such a system under given conditions can be estimated. A very prominent worker in this field has been Roozeboom, who has studied numerous systems from 1888 onwards, such as the equilibrium between water, ice, and steam, between water and sulphur dioxide, between the different hydrates of metallic salts such as ferric chloride or sodium sulphate. Roozeboom has endeavoured to depict the phase rule as a complete mechanical expression of chemical reactions, but van 't Hoff (1892) and Ostwald (1897) agree that this is pressing its utility a little too far! Nernst has expressed the general conception of the equation when he calls it a "scheme into which complete heterogeneous equilibrium fits".

The sharp change of physical properties which denotes the passage from one phase to another has been called the "eutectic point" by Guthrie (1885), but van 't Hoff's term "transition point" is of more frequent use. Guthrie's work was concerned with the investigation of mixed melting-points.

Similarly, Konowalow studied the vapour-pressure curves of various liquid mixtures in 1881, and found that three different types of curves existed: continuous, with a maximum, and with a minimum point.

Van 't Hoff (1884-92) elaborated various other means for determining the transition-point, such as the dilatometer method, observation of sudden rise or fall in temperature, and study of solubility curves; Stewart (1907) has used absorption-spectra, and Dunstan and Thole (1908) viscosity.

Other interesting examples of phase-rule systems, besides those due to Roozeboom, are the allotropic forms of sulphur (Reicher, 1884), double salt formation (Reicher, 1887; Van 't Hoff and Von Deventer, 1887), and the allotropic forms of tin (white (metallic) and grey (non-metallic), Cohen, 1899).

CHAPTER XI

THE PROGRESS OF EXPERIMENTAL METHOD

§ 1. **Improvements in Chemical Apparatus**—The conditions under which a modern chemist works are (or should be) ideal, when compared with those of a few generations ago. In a well-equipped laboratory he has a generous expanse of working space, abundance of clean, roomy drawers for his apparatus and preparations, and water, gas, electricity, and even "vacuum" laid on to his bench. The alchemists and most of the phlogistonists were "apothecaries," and pursued their researches as best they could in the back room behind the shop, aided by a spirit-lamp or a charcoal fire, some home-made glass flasks and bottles, and a water supply from the communal pump. It is true that the wealthier chemists (e.g. Cavendish or Priestley) fitted up better arranged laboratories for themselves, and not a few of the others managed to get under the patronage of aristocrats overburdened with money, but the majority of the old pioneers of our science had to shift for themselves, and thereby very possibly made readier practical chemists than the modern student who cannot blow a spherical distilling bulb for love or money. The modern research laboratory emanated from Germany, and Wöhler's at Göttingen (1830), and Bunsen's at Marburg (1840), may be regarded as the first buildings erected for practical instruction on modern lines. Such laboratories have spread enormously, of course, since then, and now, in addition to purely academic institutes, the

foremost technical works have their own research and testing laboratories, supervised by chemists.

Much time used to be wasted by chemists in collecting material as a basis for their research, but this is obviated nowadays, since several firms find it worth their while to devote themselves to the manufacture of pure chemicals for such purposes.

With reference to details of apparatus the following summary will show how comparatively recent is the introduction of numerous small inventions which at the present time seem indispensable :—

Marggraf.	Use of microscope for crystals, flame tests for sodium and potassium.
Bergman.	Use of blowpipe in mineral analysis.
Berzelius.	Perfected the use of the blowpipe (inner and outer flames, with borax, cobalt, etc.) ; introduced rubber tubing, water baths, etc.
Liebig.	Introduced the usual glass water-jacketed condenser first used as a " reflex " by Kolbe and Frankland.
Bunsen.	Introduced the Bunsen gas burner, thermo regulators, constant level water-baths, water suction pumps, systematic use of spectroscope, etc.
Beckmann.	Delicate thermometers, etc.
Anschütz.	Performed the first distillation under reduced pressure.
Crafts.	Distillation in the vacuum of the cathode light.

§ 2. **Improvements in Chemical Methods**—Dioscorides (about 100 A.D.) used to prepare quicksilver from cinnabar by *distillation*, and methods of distilling were improved by the alchemists, who could purify alcohol and ether, and the phlogistonists, who were thereby able to prepare various essential oils and esters.

Reactions of *double decomposition* were also known to the ancients and alchemists, as evidenced by the preparation of caustic alkalies, of ammonium carbonate (from potashes and sal ammoniac), and of silver chloride (from rock salt and lunar caustic). Basil Valentine separated different metals as insol-

uble salts, and, to give a modern instance, Scheele used lime or litharge to precipitate most of his organic acids from the plant-juices in which he found them.

The formation of hydrocarbons by *reduction* has already received notice (chap. vii. p. 118); other reduction processes have involved the use of hydrogen sulphide (in acid or alkaline solution, Zinin, 1842), hydriodic acid, without (Berthelot, 1867) or with phosphorus (Baeyer, 1870), sodium in the form of wire (Hofmann, 1874), of ethylate (Baeyer, 1879), of amylate (Bamberger, 1887) or of amalgam (Lippmann, 1865; Baeyer, 1892), iron filings (Béchamp, 1854), zinc in acid (Girard, 1856), neutral Lorin, 1866) or alkaline solution (Zogoumenny, 1876), tin (Beilstein, 1864), and stannous chloride (Böttger and Petersen, 1871).

Of *oxidizing* agents, in addition to the previously-mentioned ozone and hydrogen peroxide, potassium permanganate and nitric acid (Debus, 1858) have always been favourites with organic chemists. Other interesting applications have been made of chromic acid (potassium salt, Penny, 1852; the acid itself, Graebe, 1880), soda lime (first made and used in this connexion by Dumas and Stas, 1840), bromine (for sugars, Blömstrand, 1862; E. Fischer, 1889), alkaline silver oxide (Tollens, 1882), and sulphuric acid (for mercaptans, Erlenmeyer, 1861; conversion of piperidine to pyridine, Königs, 1879).

Substitution processes having played such an important rôle in organic chemistry, we will tabulate the chief methods which have been utilized in this connexion:—

Nitration—

$HNO_3 + H_2SO_4$—Schönbein, 1846; modified by Martius, 1868; Nölting, 1884; Nietzki, 1887; and others.

$HNO_3 + CH_3 . COOH$—Cosak, 1880.

Oxidation of nitroso-compound—Schraube, 1875.

$AgNO_2$ (for fatty compounds)—V. Meyer, 1874.

Methylation—

Dimethyl sulphate—Badische Anilin-Soda Fabrik.

Bromination—

Bromine in chloroform, carbon disulphide (Michael, 1866), or acetic acid (Graebe and Weltner, 1891).

Chlorination—

Cl_2 gas—"The four Dutch chemists," 1795.
Cl_2 liquid—Badische Anilin-Soda Fabrik, 1890.
Diazochlorides—Griess, 1885.
Cu_2Cl_2 and diazo-bodies—Sandmeyer, 1884.
Reduced copper and diazo-bodies—Gattermann, 1890.
PCl_5—Dumas and Péligot, 1836.
$POCl_3$—Chiozza, 1853.
PCl_3—Béchamp, 1856.
$SOCl_2$—Heumann, 1883.

Iodination—

Iodine in carbon disulphide (Schwald, 1883) or aqueous potassium iodide (Baeyer, 1885). (Application limited.)

Halogen Carriers—

Iodine (for Cl_2 and Br_2)—Müller, 1862; Kekulé, 1866.
Various metal chlorides—Perkin and Duppa, 1859; L. Meyer, 1875; Beilstein, 1876; Gustavson, 1881.
Phosphorus (for Br_2 and I_2)—Serullas, 1848; Personne, 1861.

Fluorination—

Various methods—Reinsch, 1840; Frémy, 1854; Borodine, 1862.

Sulphonation—

$(NH_4)_2SO_3$—Piria, 1850 (for nitro-bodies).
Fuming H_2SO_4—Barth, 1868 (with P_2O_5, 1871).
100 per cent. H_2SO_4—Lunge, 1889.
$K_2S_2O_7$—E. Fischer, 1877 (for phenylhydrazine derivatives).
Addition of bisulphite—Bertagnini, 1853 (aldehydes); Messel, 1871.
$Cl.SO_3H$—Limpricht, 1885.

Sulphination—

Cu powder, SO_2 and diazo-compounds—Gattermann, 1899.
SO_2, $AlCl_3$ and aromatic derivatives—Smiles and Le Rossignol, 1908.

Finally, we must refer to hydrolysis or molecular fission, effected by aqueous or alcoholic alkalies, baryta (Baeyer, 1881), silver oxide (Hantzsch, 1886), but not ammonia, on account of secondary reactions (Liebig, 1834). Sulphuric or hydrochloric acids (Lautemann, 1863; Gal, 1865) have also been used as saponifiers, while for more profound decomposition recourse has often been had to aluminium chloride (Hartmann

and Gattermann, 1892, for phenol ethers), hydriodic acid (Zeisel, 1885, for the same), or fusion with caustic alkali for alkaloids, etc. (Pelletier, Laurent, and others); Kolbe, 1860 (salicylic acid synthesis); Weselsky and Benedikt, 1878, reduction of nitro- to azo-phenols; a suitable apparatus for potash fusions was designed by Liebermann, 1888.

§ 3. **Development of Analytical Methods**—Basil Valentine separated a few metals by precipitation with suitable acids or bases, and thus recognized alloys containing copper, iron, silver, and gold. Later on Tachenius was able to give a partial scheme for separating mineral substances, using precipitation reactions, and depending largely on the colours of the precipitates. The word *analysis* was first used to describe such processes by Boyle, and he, as well as his successors, Hofmann, Marggraf, Scheele, and others, devised numerous other isolated tests for metals and acids, and mineral earths.

(*a*) *Inorganic Qualitative.*—The scattered reactions known towards the close of the phlogistic era were collected by Bergmann, who also arranged a systematic series of reagents for testing, and who, with Cronstedt and others, was instrumental in introducing the mouth blowpipe into analytical operations. Berzelius and Klaproth did much for this branch of chemistry, the extent of which in 1801 may be gathered from the handbooks of mineral analysis published at that date by Lampadius and others. Berzelius moreover introduced the modern division of metals and acids into groups, a work which has been carried on throughout the last century, notably by Rose, Fresenius, and Noyes. The separation of closely allied metals, such as the rare earths, by means of fractional crystallization of their sulphates, nitrates, oxalates, chromates, bromates (James, 1907), or acetylacetone derivatives (Urbain, 1896) also deserve mention here, and so does the general analytical work of Fenton, 1895-.

(*b*) *Inorganic Quantitative.*—The estimation of a substance in compound rather than element form was first advocated by

Bergmann, who weighed calcium as oxalate, sulphuric acid as barium salt, lead as sulphide, etc. Previous to this Marggraf had used silver chloride to determine silver in alloys, and Black had shown how to estimate magnesia as carbonate. The quantitative analysis of minerals received attention from Klaproth and from Bergmann, who decomposed silicates by alkaline fusion, but it was Berzelius who made the greatest advances here, using much smaller amounts of his substances than previous workers, and so facilitating manipulation. He taught the modern methods of filtering through thin bibulous paper, and of subsequent incineration of the filter and ash determination. He also introduced new methods for breaking up minerals, such as oxidation by nascent chlorine and evaporation with strong hydrochloric acid. New methods of inorganic quantitative work, as well as improvements in those existing, have been due more especially to Wöhler, Rose, and Fresenius. Of late electro-chemical methods have become prominent; these were introduced by Classen, and made more practicable by the use of rotating electrodes (Gooch and F. Mollwo Perkin). Sand (1907) has recently perfected the rapid separation of antimony from tin and of other metallic mixtures difficult to manipulate gravimetrically. We should also notice the recent use of silica crucibles and combustion tubes, superior to glass or porcelain in that they readily withstand sudden temperature changes, and of the crucibles devised by Gooch for rapid quantitative work, in which the use and subsequent drying and incineration of a filter-paper is avoided.

(*c*) *Organic Qualitative.*—Although in the process of burning an organic substance, van Helmont and Boyle noticed the formation of water, and Priestley detected carbonic acid gas, and Scheele observed both, yet it was left to Lavoisier to state definitely, after the erection of his oxygen theory, that carbon and hydrogen occurred in all organic bodies together, sometimes with oxygen and nitrogen. The presence of the latter element was detected by Berthollet by conversion to ammonia, and by

Lassaigne (1843) by the formation of sodium cyanide on fusion with sodium. Halogens were also detected by this means, while Berzelius usually tested for phosphorus and sulphur by oxidation with nitric acid to phosphoric or sulphuric acids. Beyond such elemental testing, there is little to be recorded here of qualitative organic analysis. As new classes of compounds were discovered and new radicles became known, methods of identifying the different groups naturally followed from a knowledge of their behaviour and nature.

(*d*) *Organic Quantitative.*—Lavoisier used to determine the amount of carbon and hydrogen in organic substances by heating them in oxygen or with mercury or lead oxides, and catching the products of combustion in suitable absorbents (he is said to have used blotting-paper to absorb the water formed!). Saussure and Thénard (1807) used potassium chlorate as oxidant, but were met with the difficulty of the violent action which thus ensued. Berzelius tried to modify this by adding common salt as a diluent, Gay-Lussac introduced the use of copper oxide in 1815 and finally Liebig about 1830 devised the combustion-furnace practically as we know it to-day. With reference to the collection of the products, Berzelius improved on Lavoisier's method for the water by substituting calcium chloride for the blotting-paper, and much more recently Mathesius commenced to use pumice soaked in strong sulphuric acid (1882), the most convenient form of apparatus being that devised by Collie (1895). The carbon dioxide has always been collected in caustic potash, different kinds of absorption bulbs having been invented by Liebig (1843), Geissler (1880), and Delisle (1891) amongst others. Other methods of oxidizing the carbon have been used by Kapfer (vapour and oxygen passed over spongy platinum, 1876), by Messinger (oxidation in the wet way by chromic acid, 1888), and by Dennstedt, who has recently perfected a furnace for rapid analyses of organic compounds.

Nitrogen has been determined as gas by the combustion method of Dumas (1830), as ammonia by Will and Varrentrapp

(heating with soda-lime, 1841) and by Kjeldahl (heating with sulphuric acid, 1883); the last method has proved very serviceable for rapid technical analyses.

Halogens have been estimated by conversion to metal halide, either by heating the substance with lime (Piria and Schiff, 1879) or by heating under pressure with fuming nitric acid (Carius, 1860), and similarly sulphur and phosphorus can be converted to sulphuric or phosphoric acids by fusion with caustic potash and nitre (Liebig, 1849) or by the Carius method. The fusion of organic substances with sodium peroxide must also be mentioned as a means of estimating either of these last elements (Edinger, 1895).

We must refer, too, to a variety of methods introduced at different periods for the estimation of particular compounds or radicles:—

Alcohol. Specific gravity (Réaumur, 1733; Brisson, 1768). Refractometer.
Sugar. Polarimeter (Clerget, 1870); also recently by refractometer.
Methoxyl, $-OCH_3$ } Heating with hydriodic acid and weighing as AgI.
Ethoxyl, $-OC_2H_5$ } Zeisel, 1885; Perkin improved apparatus, 1904.
Nitro- $-NO_2$ } Reduction by tin and volumetric estimation of unused
Nitroso- $-NO$ } metal (Limpricht, 1878).
Phenols and some other hydroxylic compounds—
(i) Formation of benzoyl derivative and hydrolysis (Schotten, Baumann, 1887).
(ii) Hydrolysis of acetyl derivative, formed by heating with acetic anhydride and sodium acetate (Liebermann, 1874).
Carboxyl group—
(i) By formation of bisulphite compound (Bertagnini, 1853).
(ii) By formation of phenylhydrazone (E. Fischer, 1877), or semi carbazide (Baeyer, 1894).
Amino group—
(i) Action of nitrous acid and measurement of evolved N_2 (Heintz, 1866).
(ii) Analysis of salts or acetyl or benzoyl compounds.

(*e*) *Volumetric Analysis.*—The founder of this very useful means of analysis was Gay-Lussac who, from 1824-32, de-

vised titration methods for the estimation of acids and bases (alkalimetry), of bleaching-powder, of chlorine, and of silver (chlorimetry), the latter depending on the reaction between a chloride and a soluble silver salt. Volhard (1874) devised the sulphocyanide method of silver titration, Marguerritte (1846) the permanganate method for iron estimation, and Bunsen (1853) the determination of iodine by sodium bi-sulphite. Improved forms of the necessary apparatus (burettes, pipettes, etc.) were brought forward, notably by Bunsen and by Mohr; and, within the past fifty years, modifications of the above half-dozen fundamental methods, too numerous for individual attention, have been arranged by a multitude of chemists so that, at the present day, there is hardly an element or a compound, inorganic or organic, which cannot directly or indirectly be brought within their scope.

Reference may be suitably made here to the work on the theory of "indicators" (i.e. the class of substances used in alkalimetry to show by their colour if the reaction-mixture is acid or alkaline), done more especially by Hantzsch, A. G. Green, A. G. Perkin, Hewitt, and Veley.

(*f*) *Gas-analysis.*—During the phlogistic period the qualitative separation of a few gases became known; thus caustic potash was used to absorb carbon dioxide and nitrogen peroxide, and moist ferrous hydroxide or phosphorus to remove oxygen. Schemes for systematically detecting various gases were, however, first brought out by Priestley, Lavoisier, Dalton, and Gay-Lussac. The qualitative side of the question was first studied by Cavendish, who used to employ explosion methods (eudiometry; hydrogen and air; nitrogen and oxygen; hydrogen and chlorine, etc.). Important work, leading up to the modern methods, was carried out by Henry, by Gay-Lussac and by Bunsen; and finally, the possibility of determining the composition of a gaseous mixture by successive removal of its constituents by suitable absorbents was realized by the gas burettes and absorptiometers of Winkler, Hempel, and Lunge 1875-90).

§ 4. **The Determination of Atomic Weights**—Reference has been made at different points in previous chapters to advances in atomic weight determination, such as the application of Dulong and Petit's law of constant specific atomic heat, of Mitscherlich's discovery of isomorphism, the more recent use of gas-densities corrected by van de Waal's constants, and Cannizzaro's rules for selecting the correct multiple of the chemical equivalent.

It is therefore intended to give here only a résumé of the accurate measurement of chemical equivalents.

Dalton based the atomic theory on relatively few and inaccurate practical data, and we are indebted to Berzelius for the greater number of satisfactory values of the equivalents of the elements then known. Some of the methods he used are quoted below, and some idea of the indefatigable nature of his work will be gathered when it is remembered that in a decade he made careful analyses of over two thousand compounds.

Another notable analyst was Dumas who, after finding discrepancies between Berzelius' numbers and his own (obtained from vapour density), and also detecting an error in the Berzelian value for carbon, applied himself in succeeding years to several equivalent determinations, using especially the precipitation of halides of the element by silver nitrate. More systematic study of the subject was entered upon by Marignac (1842-58) and Stas (1840-65), the precautions against error taken by the latter being so elaborate that for nearly forty years no one cared to question his experimental accuracy; these investigations aimed at securing a series of independent values for each element, based upon the numbers (exceedingly carefully obtained) for two or more of the following: sodium, potassium, silver, chlorine, bromine, iodine.

The more recent use of the gas constants, however, has led in the hands of Leduc (1895), Guye (1902), Gray (1905), and others to the detection of small but very perceptible errors in some of Stas' fundamental values, and in consequence of this

the redetermination of atomic weights has been attended to, both by density methods (Gray, 1905-; Guye, 1905-, etc.) and by chemical methods, in which an American school of chemists, under Clarke and Richards, has of late years been very prominent.

Our summary would not be complete without reference to the method by which the general selection of the most reliable values is made, namely, by means of an annual international commission of four distinguished workers, French, German, American and English.

We will conclude with a few instances of the chief methods of gravimetric equivalent determination which have proved serviceable:—

Precipitation of halide by silver nitrate	Ba, Sr, 1858, Marignac; As, Sb, Sn, Pb, 1856-9, Dumas; Li, 1860, Stas; Al, 1880, Mallet; Ti, 1885, Thorpe.
Conversion of sulphate to oxide	Al, 1812, Berzelius; Be, Th, 1880-2, Nilson; Cr, Cu, Zn, 1884, Baubigny.
Conversion of oxide to sulphate	Mn, 1883, Marignac; Sc, 1880, Nilson.
Conversion of chlorate, etc., to halide by heat	Cl, Br, I, 1842-6, Marignac and Stas; K, 1842-6, Marignac; Ag, 1860-5, Stas.
Conversion of element to oxide	C, 1882, Roscoe; 1885, van der Plaats; P, 1885, van der Plaats; In, 1867, Winkler.
Reduction of oxide to element	Fe, 1844, Erdmann and Marchand; Mo 1859, Dumas.
Ignition of salts, leaving element	Au, 1887, Thorpe and Lawrie; S (from silver sulphate), 1860-5, Stas; Pb, Ir Os 1878-88, Seubert.
Volume of hydrogen from metal and acid	Zn, 1884, Ramsay and Reynolds.

Numerous other devices have naturally been used, but the above are the most interesting.

We may remark upon the especially careful determinations made in the case of argon and potassium, iron, cobalt, and

nickel, and iodine and tellurium, owing to anomalies occurring in the periodic system under the present atomic weight values. In no case has the discrepancy been removed; in the last instance, many efforts have been made to ascertain whether tellurium is a mixture of elements, but the most recent and exhaustive work of Baker and of Marckwald (1907) discountenances this view.

APPENDIX A

Biographical Index of Chemists

In the following pages the scope of the work and a few other points of interest about the lives of some 150 typical chemists are briefly and it is hoped concisely summarized. The names are given, as far as possible, chronologically and in the order of the six chemical periods (chap. i. p. 4). It is to be understood that neither the workers chosen nor the accounts of their work offer in the slightest degree a complete compilation of even the leading men of our science; but possibly a clearer idea of individual contributions to chemistry will be gained by a perusal of this appendix.

Alchemical Period

Geber (end of eighth century), Arab physician and first noted alchemist. Wrote several books, which show his knowledge of the common metals, salts, acids, and alkalies, their preparation and purification (crystallization, distillation, filtration, sublimation), and his beliefs in transmutation and in mercury and sulphur as the two primal elements.

Paracelsus (1493-1541). A Swiss iatrochemist of great ability, obscured by conceit and fiery temperament. Initiated many reforms in medicine and chemistry. Introduced alcohol preparations, lead, and antimony compounds, and "vitriols" as remedies. Improved practical metallurgical methods.

Van Helmont (1577-1644), Brussels chemist of great perception. Realized that "fire" is not material; the "conservation of matter" in isolated instances; differentiated the more common gases, especially "gas sylvestre" (CO_2);

and created "physiological chemistry" by insisting on the study and importance of the reactions and secretions of the body.

Boyle, Robert (1626-91), Irishman. Studied in France, Geneva, Italy, Oxford (1654-68), and London (President of the Royal Society, 1680-91). Unbiassed, truly scientific character. Wrote several brilliant books. Defined "element," "compound," "mixture," "analysis," predicted the existence of many more elements than were then recognized, and advanced a "corpuscular" theory of matter. Investigated the relation of pressure to volume in a gas, the manufacture of various alloys, glass, and phosphorus, discovered methyl alcohol (wood-spirit), phosphoric acid, darkening of silver salts by light, improved analytical tests, etc. etc.

Kunkel, Johann (1630-1702), German Court alchemist. Believed in transmutation, but relentlessly denounced the charlatans. Improved the manufacture of various iron and copper alloys, glass, phosphorus, etc.

Becher, Johann (1635-82). Revived Geber's three principles as "terrae mercurialis, vitra and pinguis". The last gave rise to Stahl's theory of phlogiston.

Phlogistic Period

Mayow, John (1645-79), physician. Recognized (1669) that the "spiritus nitro-äereus" present in both air and nitre unites with metals on calcination.

Stahl, G. E. (1660-1734), Prussian court physician. Trained a number of eminent chemists, and devised his phlogiston theory to explain oxidation and reduction processes.

Hoffmann, Friedrich (1660-1742), Prussian professor. Views similar to Stahl's on combustion, but resembling others on calcination. Developed qualitative analysis, and investigated many mineral waters.

Rouelle, G. F. (1703-70). Taught Lavoisier and Proust. Defined neutral, acidic, and basic salts (1744); discovered urea (1737), sulphuretted hydrogen and other compounds.

Marggraf, A. S. (1709-82), pupil of Stahl and German professor. Noted increase in weight on oxidation of

phosphorus; discovered beet-sugar (1747), alumina (as distinct from lime, 1754), and introduced the microscope into analysis; estimated silver as chloride and knew the flame tests for the alkalies.

Black, Joseph (1728-99), Scottish professor. Worked at latent heat (1762), specific heat, thermometry, calorimetry, and elucidated nature of CaO, MgO, NaOH and their carbonates. Supported Lavoisier's oxygen theory in preference to that of phlogiston.

Bergmann, T. (1735-84), Swedish professor. Important for his views on chemical affinity (1777), development of mineral analysis (blowpipe, systematic tests, gravimetric methods for Ca, H_2SO_4, Pb, etc.), discovery of molybdenum and tungsten, 1778, and theory of "vital force" for organic compounds.

Scheele, C. W. (1742-86), Swedish apothecary. Pioneer in nearly every branch of chemistry, with great power of observation. Discovered, amongst other substances, oxygen (1774), chlorine, manganese (1778), barium (distinct from lime), phosphoric acid in bones, fluorine, hydrogen persulphide, arsine; and in organic chemistry, glycerol (1779), aldehyde (1774), and tartaric (1769), uric and oxalic (1776), lactic and pyromucic (1780), prussic (1782), malic (1785), pyrogallic (1786), and citric acids; improved qualitative analysis, developed actinic and pneumatic chemistry, etc. A confirmed phlogistonist.

Priestley, Joseph (1733-1804), theologian and chemist. Staunch upholder of the phlogistic theory. Lived at Birmingham and subsequently died in America. Immensely enriched pneumatic chemistry; used mercury for collecting gases, invented the pneumatic trough; discovered ammonia gas, nitrous and nitric oxides, oxygen (1774); isolated SO_2; showed that burning organic bodies produced carbonic acid; regarded hydrogen as "phlogiston".

Richter, J. B. (1762-1807). Invented the term "stoichiometry," and exactly determined the equivalents of various compounds, especially in reactions of "double decomposition". Obscured the value of his results by expressing them phlogistically.

Cavendish, Henry (1731-1810), English philosopher. In-

vented eudiometry and studied the volumetric composition of water, nitric acid, air, etc. Discovered hydrogen (1773); estimated the density and weight of the earth; like Priestley and Scheele, in spite of his own anti-phlogistic work, he always subscribed to the phlogistic theory.

Modern (Fundamental) Period

Lavoisier, Antoine (1743-1794), mathematician, physicist, and chemist. Great politician; "Fermier-General". Murdered by the French Revolutionary Court. Insisted on accurate measurements and attention to the weights of reacting substances. Showed that metal "calces" were heavier than the metals producing them (1772); proved the "conservation of matter" (1774); investigated oxidation of P, S (1772), Sn (1774), Hg, etc. (1775); replaced "phlogiston" by "oxygen" (1777); systematized the terms acid, base, organic compound, salt, etc. Devised the combustion process for analyzing organic substances. Improved gas-analysis; gave hydrogen and oxygen their present names; quantitatively synthesized water (1783); damaged his reputation by trying to rob Priestley and Cavendish of the merit of their respective discoveries of oxygen and the compound nature of water.

Morveau, G. de (1733-1816), Professor at École polytechnique, Paris, and friend of Lavoisier. Introduced the first systematic nomenclature for chemical substances, 1782; showed that soda-crystals could be made from Glauber's salt by heating with coke and iron.

Berthollet, C. L. Count (1748-1822), Professor in Paris. Chemist under Napoleon in Italy and Egypt. Renounced the phlogiston theory in 1785; investigated ammonia, prussic acid, sulphuretted hydrogen, and chlorine ("oxymuriatic gas"); used sodium hypochlorite solution as bleaching agent ("Eau de Javelle," 1800); believed mass to be the predominant factor in chemical change, 1801; controversy with Proust on the law of multiple proportions, 1801-7.

Proust, J. L. (1755-1826), Parisian apothecary and later professor in Spain. Noted for his work just mentioned, in

which by means of basic copper carbonates, oxides of tin and iron, and sulphides of iron, he established the law of multiple proportions. Also worked at organic chemistry.

Fourcroy, A. F. (1755-1800), Professor in Paris. Advanced animal and mineral chemistry.

Vauquelin, L. N. (1763-1829), Professor in Paris. Discovered various elements (Be, and Cr, 1797), many naturally-occurring organic compounds (asparagine, 1805; camphoric and quinic acids, etc.), and cyanic acid (1818).

Wollaston, W. H. (1766-1829), English physicist and chemist. Worked at emission and absorption spectra (1802), discovered some of the platinum metals (1803-4), some organic substances (cystine), and regarded Dalton's atoms as "equivalents" only (1814).

Klaproth, M. H. (1743-1821), first Professor of chemistry at Berlin. Discovered strontium (1790), zirconium, tellurium (1798), uranium and cerium (1803), composition of honeystone (aluminium mellitate, 1799). Improved mineral analytical methods considerably.

Dalton, John (1766-1844), Teacher at Manchester. Discovered colour-blindness (1793), composition of carbon dioxide (1803), and olefiant gas, etc., law of partial pressures (1807), and enunciated his atomic theory (1807-8); invented a system of elementary symbols.

Davy, Sir H. (1778-1829), English chemist. Worked at nitrous oxide and phosphorus pentachloride (1800); isolated electrolytically the metals of the alkalies (1807) and alkaline earths (1808); electro-chemical theory, 1807; elementary nature of chlorine (1810); chlorine oxides, complex acids, miners' safety-lamp, chemistry of flame and actinometry.

Gay-Lussac, J. L. (1778-1850), Professor at Paris. Taught by Berthollet. Worked at inorganic chemistry (halides of nitrogen and phosphorus, etc., 1800); gas analysis and physical research (1801-8); law of volumes, 1808; chlorine, 1810; introduced copper oxide in the combustion process, 1815; complex inorganic acids, 1815-20; cyanogen, 1815-22; invented volumetric analysis (acid and alkalimetry, silver, chlorine, 1824-32); improved manufacture of oxalic (1829) and sulphuric acids (1827).

Prout, J., English physician. Supposed all atoms to be polymers of hydrogen, 1815. Also worked at organic products of the metabolism.

Berzelius, J. J. Baron (1779-1848), Swedish apothecary, professor (1802) and secretary (1818) to the Stockholm Academy of Sciences. His chief aim was the final establishment of the laws of chemical proportion, including the determination of atomic weights and the constitution of inorganic and organic compounds. Discovered cerium (1803), selenium (1817), thorium (1828), isolated Si (1810), Zr (1824), Ti (1825); worked at many inorganic compounds, notably those of the rarer metals, such as Ti, Zr, Th, Cr, Mo, W, U, V, etc. Elaborated what is practically the present system of nomenclature and symbols for inorganic compounds in 1811, put forward his electro-chemical (dualistic) theory in 1812, and extended it in 1819; drew up a table of atomic weights in 1817, and a modified one in 1826; discovered sarcolactic (1807), racemic (1832), and pyruvic acids (1835) as well as many other organic compounds; defined iso-, poly- and meta-merism, 1831; contact theory of fermentation, 1834; vastly improved analytical methods and general manipulation (introduced use of rubber tubing, water baths, gravimetric filter-papers, borax, cobalt, and other blowpipe reagents, etc.).

Dulong, P. L. (1785-1838), Director of École polytechnique, Paris. Worked on oxides of nitrogen (1816) and the reduced oxy-acids of phosphorus (1818); discovered constancy of specific atomic heats (1821).

Mitscherlich, E. (1794-1863), Professor at Berlin (1821-63). Discovered isomorphism (1819) and polymorphism (1821). Investigated substitution (benzene sulphonic acid, 1833; nitrobenzene, 1834), benzene from benzoic acid (1834), the oxides of manganese, lactic acids, and the allotropes of sulphur (1852). Put forward a contact theory of fermentation (1836), and ascribed the formation of ether from alcohol to catalysis.

Thénard, L. J. (1777-1857), Professor at École polytechnique, Paris. Worked at first in conjunction with Gay-Lussac on processes for manufacturing bleaching-powder (1799), white lead (1801), and chlorine (1810), discovered H_2O_2 (1818),

HF, phosphorus hydrides and preparation of organic phosphines (1845-8).

Modern (Static Structural) Period

(*a*) *General and Physical*

Faraday, Michael (1791-1867), Assistant to Sir Humphrey Davy, and later his successor at the Royal Institution. Discovered liquefaction of gases, 1823; butylene and benzene, 1825; actinometry; laws of electrolysis, 1833; discovered magnetic rotation of polarized light, 1846.

Regnault, H. V. (1810-78), Professor at Aix-la-Chapelle and Paris. Worked on the composition of various alkaloids (1840 and 1860); established the constitution of piperine, 1863; aliphatic sulphonic acids, 1840; put forward the theory of "mechanical organic types"; variation of specific heat with temperature, 1840; measurements of densities (1845) and specific heats (C_p and C_v, 1853) of gases.

Deville, H. St. Clair (1818-81), Professor at Paris. Investigated inorganic compounds (N_2O_5, 1849; halides of B, Si, etc.; preparation of metals from their chlorides heated with sodium; purification of the platinum metals, 1805-9) and physical properties (refractive index, 1854; dissociation on heating, 1857).

Pasteur, Louis (1822-95), Professor at Strassburg. Investigated optical activity (enantiomorphous sodium ammonium tartrate crystals, 1850; resolution of racemates by mechanical means, 1850; by fractional crystallization with active base or acid, 1853; by bacteria, 1860; isogonism, 1861) and biochemistry (vitalistic fermentation theory, 1855; bacteriology, 1865-95; Institut Pasteur at Paris opened, 1889).

Kopp, H. (1817-92), Professor at Giessen. Pupil of Liebig. Worked chiefly on specific volumes (1842-1855), boiling-points (1845-60), and variation of specific heat with temperature (1865).

Cannizzaro, S., Italian professor. Faraday lecture, 1872. Established rules for determining which multiple of the

equivalent is the atomic weight, 1858. Other work mainly organic.

Thomsen, J. (1826-1908), Danish professor (Copenhagen). Extremely thorough and varied thermo-chemical investigations (1853-1908).

Berthelot, M. (1827-1907), Parisian professor and Secretary of State; chemical historian. His work embraces four periods: (*a*) 1850-60, constitution and synthesis of polyatomic fatty alcohols and acids; (*b*) 1861-69, pyrogenetic and electric arc syntheses of hydrocarbons (acetylene, benzene, etc.); reduction to hydrocarbons by hydriodic acid; (*c*) 1869-85, extensive thermo-chemical investigations, especially dealing with explosives; silent electric discharge syntheses; (*d*) 1885-1907, agricultural and historical chemistry.

Gladstone, J. H. (1827-1902), President Chemical Society, 1877. Refractive index of elements and specific refractive index, 1858; atomic weights, refraction and dispersion investigations, 1860-1902.

Landolt, H., Professor at Berlin. Organic As and Sb compounds, 1853; formula for refractive index, 1864; connexion between refractive index and periodic law; optical activity of electrolytes, 1863; conservation of matter re-proved, 1893-1908.

Meyer, J. Lothar (1830-95), Professor at Karlsruhe and Tübingen. Chemistry of blood, 1857; molecular volumes and periodic system, 1867-70; compounds of halogens with each other, 1877-85.

Mendelejew, D. I. (1834-1907), Professor at St. Petersburg, 1865. Work on expansion of liquids, 1861; periodic system, 1869; critical data of gases, 1870-85; voluminous author.

Horstmann, A. Thermo-dynamics of law of mass action, 1869-77; stated the simple gas equation $PV = RT$; specific volumes (1886-88).

(*b*) *Inorganic*

Balard, M. (1802-76). Discovered bromine, 1826; constitution of bleaching-powder, 1835.

Graham, T. (1805-69), Professor at Glasgow and University College, London. President Chemical Society, 1841. Polybasicity of phosphoric and arsenic acids, 1833; diffusion, dialysis, and osmosis (of liquids) and diffusion and effusion (of gases), 1851; definition of crystalloids and colloids, 1862.

Rose, H. (1795-1864), Professor at Berlin. Hydrolysis of strong acids, 1848; cobalt ammonia salts, columbium (discovered 1846); mineral syntheses and improved analytical methods.

Stas, J. S. (1813-91), Professor at Brussels. Very exact determinations of atomic weights, 1840-70; toxicological tests, 1850; spectra of alkaline earths, 1880.

Marignac, J. C. G. (1817-94), Professor at Geneva. Constitution of ozone; thermo-chemistry and atomic-weight estimations (1842-83).

Roscoe, Sir H., Professor at Manchester. President Chemical Society, 1880. Complex inorganic acids; isolation and compounds of W, V, etc., 1867; actinometry, 1857; spectroscopic work, 1863; atomic weights, etc.

Winkler, C. (1838-1904), Professor at Freiburg. Gas-analysis; hydraulic cements; contact-process for H_2SO_4, 1875; discovery of germanium, 1886; atomic weights, etc.

Boisbaudran, Lecoq de, Professor at Paris. Discovered Ga, 1875; Sm, 1879; Dy, 1886; Gd, 1889; mathematical relations of spectra, 1889.

Nilson, L. F. (1840-99), Professor at Stockholm. Discovered Sc, 1879; atomic weights (Be, Th, Sc, 1880-2); specific heats (Dulong-Petit Law) and vapour densities at high temperatures, 1880-9.

(*c*) *Organic*

Döbereiner, J. W. (1780-1849), Professor at Jena. Relation of acetic and oxalic acids to alcohol, 1821; noted series of "triads" in the metals (e.g. Ca, Sr, Ba, 1829); discovered furfurol, 1831; worked on aldehyde, 1834.

Dumas, J. B. A. (1800-84), Apothecary at Geneva and later professor at Paris. Vapour-density estimation, 1827; etherin theory, 1828; estimation of organic nitro-

gen, 1830; cinnamyl derivatives, 1834; substitution, 1834; hydrolysis of nitriles to acids and amines, 1847; atomic weights (1856-9); compositions of terpenes, etc.

Liebig, J. von Baron (1803-73), Professor at Giessen (1824), Munich (1852). Chief work: on fulminates with Gay-Lussac (1821), synthesis of urea (1828), chloroform (1831), on radicle "benzoyl" (1832), first radicle theory (1832), in conjunction with Wöhler; polybasicity of acids (1839); vibration theory of fermentation (1839); investigated many other organic reactions and compounds during the next twenty years, especially among the alkaloids (1837-41) and animal products such as amino-acids and amides (1846-52); in later years became more of a physiologist than a chemist.

Wöhler, F. (1800-82), Professor at Göttingen (1836). Besides his work with Liebig, he isolated Be, Al, B and Si (1828); discovered amygdalin (1837), parabanic acid (1838), hydroquinone (1848), calcium carbide (1862), etc.; worked on metallic sub- and per-oxides, non-metallic hydrides and halides, and pointed out the analogy of silicon to carbon in organic compounds (1863).

Laurent, A. (1807-53), Professor at Bordeaux. Discovered anthracene (1832), anthraquinone (1835), phthalic acid (1836), adipic acid (1837), piperine (1840), etc. "Nucleus theory," 1837; definition of equivalent, atom, molecule, 1843; ether and alcohol correspond to oxide and hydrate, 1846.

Gerhardt, C. (1816-56), Professor at Montpellier and Strassburg. Theory of residues, 1839; of four types, 1853; atomic weight system; homologous series, 1844; discovered quinoline (1842), the anilides (1845), acid chlorides from $POCl_3$ (1851) and acid anhydrides (1852).

Péligot, E. M. (1811-90), Professor at Paris. Worked with Dumas on "cinnamyl" (1834); used PCl_5 for chlorination, 1836; isolated various metals of the uranium group.

Pélouze, J. Worked on the terpene series (discovered borneol, 1841); inorganic esters of alcohol; manufacture of plate-glass, 1856.

Cahours, —. Died in 1891. Discovered amyl alcohol, 1837; anisol and its derivatives, 1841; phellandrene, 1841;

methyl salicylate (in oil of winter green), 1843 ; preparation of acid chlorides by PCl_5, 1846; allyl alcohol, 1856; tintetraethyl, 1860; alkyl sulphonium bases, 1865.

Piria, R., Professor in Italy. Discovered salicin (1839) and worked out the chief salicyl derivatives; sulphonation by ammonium sulphite (1850); and estimation of organic halogens in the dry way (1879).

Zinin, N. (died 1880), Professor at St. Petersburg. Aniline from nitrobenzene by ammonium sulphide, 1841; α-naphthylamine, 1842; benzidine from nitro-benzene, 1845; azoxybenzene, 1853.

Anderson, T., Professor at Glasgow. Discovered pyridine in bone-oil, 1846; constitution of piperine, 1850; preparation of pyrrol, 1858; constitution of anthraquinone, 1861.

Kolbe, H. (1818-84), Professor at Marburg (1851) and Leipzig (1865). Synthesis of acetic acid, 1842; methyl sulphonic acid, 1845; electrolysis of fatty acids, 1850; nature of valency, 1854-65; synthesis of salicylic acid (from phenol), 1860; taurine, 1862; malonic acid, 1864; aliphatic nitro-compounds, 1872.

Hofmann, A. W. von (1818-92), Professor at College of Chemistry, London (1845); Berlin (1865). President of Chemical Society, 1861; founded the Deutschen Chemischen Gesellschaft, 1868. Amines from ammonia and alkyl iodides, 1850; constitution of aniline, 1843; alkylanilines by alkylation, 1872; isonitriles from chloroform and amines, 1866; myrosin and mustard oil constitution, 1868; vapour density method, 1868; discovered hydrazobenzene, 1863; diphenylamine, 1864; formaldehyde, 1868, etc. etc. Prepared numerous dyes (chrysaniline, 1862; alkyl rosanilines, 1867-75; magdala red, 1869; chrysoïdine, 1877), improved methods of organic preparation and analysis, etc.

Wurtz, C. A. (1817-84), Professor in Paris. Wrote several noted chemical books; discovered $POCl_3$, 1847; ethylene oxide, 1859; reaction of amine-formation from alkyl isocyanates, 1848; action of sodium on alkyl halides, 1855; reduction of aldehydes to alcohols, 1866; and the aldol condensation, 1872.

Frankland, Sir E. (1825-99), Professor in Manchester and London. President Chemical Society, 1871. Worked on

metallo-organic compounds, 1849-64 ; theory of atomicity (valency), 1853-60 ; hydrocarbons from zinc alkyls, 1849 ; constitution of acetoacetic ester, 1864 ; helped to devise the modern structure notation, 1867.

Strecker, A. (1822-71), Professor at Würzburg. Chief work on amino-acid or peptide derivatives. Syntheses of amino-acids from 1860 ; worked on the constitution of guanine, caffeine, quinine, etc. ; introduced the method of ester-preparation from alkyl halide and silver salts of organic acids, 1861.

Williamson, A. W. (1824-1904), Professor at University College, London. Formation and constitution of the ethers, 1850-52 ; synthesis of glycol, 1854 ; formation of aldehydes and ketones by distillation of calcium salts.

Debus, H., Lecturer at Guy's Hospital. Thorough researches on the oxidation of alcohol (1856) and the composition of gases evolved from explosives.

Perkin, Sir W. H. (1838-1907), President of the Chemical Society, 1883 ; oxidation of aniline and production of mauve, the first coal-tar dye, 1856 ; synthesis of tartaric acid, 1861 ; of coumarin, 1865 ; of cinnamic acid (" Perkin's reaction "), 1875 ; constitution of salicin, 1868 ; relation between magnetic rotatory power and chemical constitution, 1892-1907.

Kekulé, A. (1829-96), Professor at Geneva (1858) ; Bonn (1865). Added the methane type to the four types of Gerhardt, 1857 ; tetravalency of carbon, 1858 (shared with Couper) ; benzene theory, 1867 ; azo-formula for diazo-salts, 1867 ; possible oscillation of the fourth valency in the benzene ring, 1872 ; syntheses of acetylene (from fumaric acid electrolysis, 1864), benzoic acid ($Na + CO_2 + C_6H_5Br$, 1866), crotonaldehyde and triphenylmethane, 1872.

Bunsen, R. W. (1811-99), Professor at Marburg (1838), Breslau, and Heidelberg (1858). Investigated cacodyl ($As(CH_3)_2$) compounds, 1837-43 ; production of cyanides from alkalies and coal, 1847 ; method for iodine titration, 1853 ; actinometry, 1857 ; distinctive emission spectra of each element, 1859 ; discovery of rubidium and caesium, 1861 ; invented many practical devices, e.g. his gas-burner, thermostats, water pumps, etc. etc.

Blömstrand, C. W. (1826-97). Constancy of valency, 1860-65; complex metallammines; "diazonium formula" for diazo-salts, 1875.

Butlerow, A. M. (1828-86), Professor at St. Petersburg. First synthetic hexoses "methyleneitan," 1861; production of tertiary alcohols from zinc alkyls and acid chlorides, 1864; isomeric butylenes and tautomerism, 1877.

Friedel, C. (1832-99), Professor at Paris. Synthesis of minerals; reduction of ketones to secondary alcohols, 1862; silicon tetra alkyls, 1863; action of aluminium chloride on aromatic hydrocarbons with alkyl halides, 1877.

Fittig, R. (1835-), Professor at Tübingen. Discovered pinacone reaction, 1858; action of sodium on mixed anyl and alkyl halides, 1863; synthesis of mesitylene, 1868; of ketonic esters by zinc dust and chlorofatty acid esters on oxalic ester, 1887; coumarone, 1883; lactones and paraconic acids (1894-1904).

Griess, J. P. (1829-88), Chemist at Burton-on-Trent. Discovered diazo-compounds, 1859-63; diazo-amidobenzene, 1862; diazobenzeneamide, 1866; Bismarck brown, 1867; congo yellow, 1889; constitution of betaïnes, 1867; orientation determination, 1872.

Erlenmeyer, E., sen. (died in 1909), Professor at Frankfurt. "Affinity points" cause valency, 1863; constitution of napthalene, 1866; final modern structure notation, 1867; synthesis of tyrosine, 1882; lactone theory, 1880; on cinnamic and iso-cinnamic acids, 1890- ; relations between isomeric fatty acids, 1898.

Lossen, W. (1838-1907), Professor at Königsberg. Discovered hydroxylamine, 1865; stereo-isomeric imido-ethers, 1872; specific volumes, 1882.

Saytzew, A. Sulphoxides and sulphones, 1866; first lactone (butyro-lactone), 1873; zinc dust as condensing reagent, 1875; palladium hydride, 1872.

Körner, W., Professor in Italy. Formula for pyridine, 1869; orientation determination, 1874; synthesis of asparagine, 1887.

Liebermann, C., Professor at Berlin Technical College. Action of nitrous acid on phenols and secondary amines, 1874; anthraquinone and oxyanthraquinones (alizarin), 1868-80;

constitution of anthracene and phenanthrene, 1870; quercitrin, 1879; work on azo-, alizarin-, anthracene and natural dyes.

Gräbe, C., Professor at Geneva. Synthesis of alizarin, 1869; acridine, 1871; carbazole, 1872; constitution of anthracene and phenanthrene, 1870; quinoline, 1878; euxanthone, 1880 (synthesis, 1889); on acenapthenes, 1893; condensations with *o*-amidobenzophenones, 1895; constitutions of acid decomposition products of plant dyes, 1899-.

Ladenburg, A., Professor at Breslau. "Prism formula" for benzene, 1869; equivalence of hydrogen atoms in benzene, 1874; orientation, 1875; aromatic silicon derivations, 1874; benzimidazoles, benzoxazoles and glyoxalines, 1875-8; synthesis of ptomaines, 1886; of optically-active coniine, 1886; on the constitution of atropine and other alkaloids, since 1880.

Jörgensen, S. M., Professor at Copenhagen. Detection of alkaloids by polyiodides, 1870; constitution and properties of metallammino (cobalt) salts, 1880-1908 (controversy with Werner).

Volhard, J., Professor at Halle. Synthesis of sarcosine (1862) and creatine (1869); thiocyanate titration for silver (1874); thiophenes from succinates and P_2S_3 (1885).

Nietzski, R., Professor at Basel. Aniline black, 1876; preparation of quinones, 1877; theory of colouring matters, 1879; Biebrich scarlet, 1880; hexaoxybenzene compounds, 1885.

Modern (Dynamic Structural) Period (Arranged Alphabetically)

(*a*) *General and Physical*

Arrhenius, S., Professor at Stockholm. Ionic theory of electrolytic dissociation, 1886; hydration of ions, 1888; conductivity of pure water, 1893; viscosity of electrolytes, etc.

Brühl, J., Professor at Heidelberg. Many investigations into the effect of constitution on refractive index, 1880- ;

constitutions of terpene derivatives, 1890; refractivity of benzene, 1894; of tautomeric substances, 1899, etc.

Dewar, Sir J., Professor at Royal Institution. President Chemical Society, 1897. Formula for quinoline, 1871; on liquefaction of gases, 1884- ; "vacuum vessel" for holding liquid air, etc.; liquefaction of hydrogen, 1898; charcoal as gas absorbent at low temperatures, 1905.

Guye, P. A., Professor at Geneva. Theory of quantitative optical rotatory power, 1890; work on "asymmetry product," 1891-9; atomic weights from gas-densities and determination of critical data, compressibilities, etc., 1900- .

Nernst, W., Professor at Göttingen and Berlin. Diffusion theory of solutions, 1888; dissociation of pure water, 1894; dielectric constant determination, 1894; quadrant electrometer, 1896, etc.

Ostwald, W., Professor at Leipzig. Nobel prize, 1909. Pycnometer and other physico-chemical apparatus, 1873- ; partition of a base between two acids (dilatometry and refractive power), 1878; rate of hydrolysis of salts and esters, 1883; conductivity of acids, 1878-87; various methods of comparing the relative "affinities" (affinity-constants) of acids, bases, etc., 1885- ; viscosity of solutions, 1891; definition of properties (additive, constitutive, colligative), 1891; conductivity of pure water, 1893.

Pope, W. J., Professor at Manchester and Cambridge. Synthesis of asymmetric (optically-active) nitrogen (1899), tin (1900), sulphur (1900) and selenium (1902) compounds; crystallographic theory, 1906; gold and platinum alkyls, 1908.

Ramsay, Sir W., Professor at University College, London. Nobel prize, 1904. President of Chemical Society, 1907. Synthesis of pyridine, 1877; atomic weight of zinc, 1884; improved Hofmann's vapour-density method (application to varying temperatures and pressures), 1885; surface-tension and molecular weight, 1893; critical data, 1894; the rare gases, 1893-1908; radio-activity, 1903- ; degradation of heavy elements to lowest member of their series, 1907- ; electronic theory, 1908-9; radium emanation or niton, 1910.

Rayleigh, Lord. Nobel prize, 1904. Composition of water, 1889; re-determination of gas densities, 1892- ; discovery of argon, 1894; and other physical researches.

Tschugaeff, L., Professor at Moscow. Optical rotatory power in homologous series, 1898; effect of *o*-, *m*-, *p*-substitution on optical activity, 1898; triboluminescence, 1901-5; work on terpenes, 1904- .

Van 't Hoff, J. H., Professor at Amsterdam. Stereochemistry of carbon (1874) and nitrogen (1878); development of law of mass-action, 1877; physical chemistry of dilute solutions, 1880; "Études de dynamique chimique," 1884; elevation of b. p. and depression of f. p. proportional to change of vapour pressure, 1886; methods for determination of transition-point, 1884-92, etc.

Van der Waals, J., Professor in Holland. Gas-equation, 1881; on electrolytic dissociation formula, 1891; capillarity, 1894; continuity of gaseous and liquid states, 1899; theory of mixtures, 1906.

Walker, J., Professor at Edinburgh. Electrolytic synthesis of malonic esters, 1891; periodic system work, 1891; hydrolysis of esters, 1889-93; boiling-points of homologous compounds, 1894; conductivity of weak acids, 1900; amphoteric electrolytes, 1902, etc.

Walden, P., Professor at Riga. Conductivity of organic acids, 1891; "Walden inversion," 1895; unsaturation and optical activity, 1896; conductivity of non-aqueous solvents, 1901-6; dielectric constants, 1906- , etc.

Young, S., Professor at Dublin. Investigations on vapour-pressure, 1886-92; relation of boiling-points, molecular volumes, and other properties and chemical constitution, 1890; critical data, 1893-4; separation of mixtures by distillation, 1894-7.

(*b*) *Inorganic*

Crookes, Sir W. President Chemical Society, 1867. Discovered thallium, 1861; phenomenon of cathode rays, 1880; spectroscopic work on rare earths since about 1880; theories of ultimate genesis of matter—"protyle," 1886; "meta-elements," 1889; fixation of nitrogen, 1892.

Curie, M. (1859-1906) *and Mme.* (Professor at Paris, in her husband's place). Radioactivity of uranium and thorium minerals, 1902; isolation of radium, 1903; polonium, 1903; disintegration of radium, 1904- . M. Curie was also noted as physicist and crystallographer.

Lobry de Bruyn, C. A. (1857-1904), Professor at Amsterdam. Nitro-aromatic compounds, 1890; hydroxylamine, 1891; hydrazine hydrate, 1894, (anhydrous), 1896; colloidal solutions, 1902.

Moissan, H. (1852-1907), Professor at Paris. Nobel prize, 1906. Metal oxides, 1879-83; fluorine compounds, 1883; isolation of fluorine, 1886; electric furnace, 1892; metal carbides and carborundum, 1893-4; nitrides; artificial diamonds; reduction of refractory metal oxides, 1896; silicon hydrides, 1902.

(*c*) *Organic*

Anschütz, R., Professor at Bonn. On pyrocondensations, 1878; oxidation of fumaric and maleic to racemic and mesotartaric acids, 1880; citraconic and isomeric acids, 1881; aluminium chloride syntheses, 1884; stereoisomeric hydrazones, 1895.

Armstrong, H. E., Professor at South Kensington. President of Chemical Society, 1893. Constitution of terpenes and camphors, 1871-96; "centric" formula for benzene, 1892; origin of colour, 1893; electric conductivity and theories of solution, 1892-1902; naphthalene-sulphonic acids, 1891; Caro's acid, 1902.

Baeyer, A. (1835-), Professor at Berlin and Munich. On polymethylenes, 1861-; constitution of furfurol and pyrrol, 1870; indene, 1884; orientation of phthalic acids, 1871; reduction of benzene and benzoic acids, 1887-92; strain theory of carbon ring-stability, 1885; steric formula for benzene, 1888; centric formula, 1892; on purine derivatives and uric acid, 1863-70; indigo constitution and synthesis, 1866-90; terpenes, 1890-1900, etc.

Bamberger, E., Professor at Munich. Guanidine and cyanamide compounds, 1880; constitution of retene, 1884; chrysene, 1895; sodium and amyl alcohol as reducing

agent, 1887; diazo-controversy with Hantzsch, 1895-1900.

Beckmann, E., Professor at Erlangen. On iso-nitroso compounds, 1886; equivalence of nitrogen valencies, 1885; isomeric benzaldoxines, 1885; apparatus and thermometer for molecular weight by freezing-point (1888) and boiling-point methods (1889), etc.

Bernthsen, A. Badische Anilin u. Soda Fabrik. Methylene-blue constitution, 1883; safranine, 1885; thiodiphenylamine and phenazine syntheses, 1886; acridines, 1884-93; hydrosulphurous acid, 1905.

Bischoff, C. A. (1855-1908), Professor at Riga. Syntheses of aliphatic acids by ketonic esters, 1876; on ring-formation, 1880-88; stereochemistry of nitrogen atom, 1890; steric hindrance, 1894.

Brown, A. Crum, Professor at Edinburgh. President of the Chemical Society, 1891. Contributions to modern structure rotation, 1865; thetines, 1878; quantitative hypothesis for optical rotatory power, 1891; electrolytic syntheses of malonic esters, 1891; osmotic pressure, 1900.

Caro, H. Induline dyes, 1865; Bismarck brown, 1867; acridine synthesis, 1871; eosin, 1873; monopersulphuric acid, 1898.

Claisen, L., Professor at Kiel. Aromatic ketonic esters, 1880; benzalacetone, 1881; pyrazole synthesis, 1888; β-diketones, 1889; tautomeric substances, 1893-99.

Collie, J. N., Professor at University College, London. Action of heat on complex ammonium and phosphorium salts, 1881-1888; on the rare gases, 1896; space formula for benzene, 1897; pyrones, quadrivalent oxygen, polyketides, etc., 1891-1907; decomposition of CO_2 by silent electric discharge, 1901.

Curtius, T., Professor at Heidelberg. Diazoacetic ester, 1883; hydrazine, 1887; hydrazoic acid, 1890-93; pyrazoline derivatives, 1894; aldazine transformations, 1900; glycocoll, asparagine and polypeptide syntheses, 1904.

Fischer, Emil, Professor at Berlin. Constitution of rosaniline and alkylrosanilines, 1867-75; phenylhydrazine, 1875; phenylhydrazones, 1877; indol and indazoles, 1885; sugars, constitutions and syntheses, 1884-1900; alkyl glucosides, 1893; configuration of pentoses, hexoses,

and tartaric acid completed, 1894; constitution and syntheses of the purines, 1881-1901; syntheses of polypeptides, 1900; discovery of proline, 1899.

Gattermann, L., Professor at Heidelberg. On nitrogen chloride, 1888; alkylene phenol ethers, 1889; liquid crystals, 1890; copper powder and diazo-compounds, 1890; electrolytic reduction of nitro-compounds, 1893; sulphination by diazo-compounds, 1898; thio-anilides, 1899; aldehydes by Grignard reagent, 1904.

Hantzsch, A., Professor at Leipzig. Pyridines from aldehyde ammonia, 1882; coumarone syntheses, 1886; theory of stereo-isomeric oximes, 1890; phenylnitromethane and conductivity of ψ-acids and ψ-bases, 1896; hyponitrous acid, 1896.

Haller, A., Professor at Paris. Syntheses from cyano-fatty esters, 1888; on camphor and borneol, 1889-1906; constitution of camphoric acid, 1893; partial syntheses of borneol (1891) and camphor (1895); effect of unsaturation (1899) and ring-formation (1905) on optical activity.

Kipping, F. S., Professor at Nottingham. Hydrindene derivatives, 1893-1904; sulphonic derivatives of camphor, 1895; keto-hexamethylenes, 1897; organic silicon derivatives, 1904-.

Knoevenagel, E., Professor at Heidelberg. Dihydroresorcinol, 1894; δ-diketones, 1894; terpene syntheses, 1896; condensation of aldehydes and malonic ester, etc., by weak bases, 1899; pyridine syntheses, 1898; moto-isomerism, 1903; sulphination, 1908.

Knorr, L., Professor at Jena. Pyrazolone and antipyrine syntheses, 1883; quinoline syntheses, 1886; pyrazole synthesis, 1887; tautomerism of methylpyrazole and of benzene, 1894; morphine alkaloids, 1890; tautomerism of diacylsuccinic esters, 1896- .

Le Bel, J. Stereochemistry of carbon, 1874; attempts to make optically active benzene compounds, 1882; stereochemistry of nitrogen, 1891; optically active asymmetric nitrogen, 1900.

Marckwald, W., Professor at Berlin. Furfurane compounds, 1888; glyoxalines, 1892; tautomerism, 1895; stereo-

chemistry of nitrogen, 1900; optical activity without atomic asymmetry, 1906; radio-activity, 1903- .

Menschutkin, N. (1842-1907), Professor at St. Petersburg. Contributions to law of mass action (velocities of ester-formation and other organic reactions; effect of constitution on the rate of reaction).

Meyer, Victor (1848-97), Professor at Heidelberg. Aliphatic nitro-compounds, nitroso-compounds and nitrols, 1872; vapour-density method, 1878; iso-nitroso-compounds, 1882; thiophene, 1883; isomeric oximes, 1883; steric hindrance, 1891-4; esterification and saponification "laws," 1895; iodoso-, iodo- and iodonium compounds, 1895.

Perkin, W. H., Professor at Manchester. Berberine, 1889; tetramethylene compounds, 1894; hexamethylene synthesis, 1894; oxidation-products of camphor, 1895-1902; braziline and haematoxylin, 1900-7; syntheses in the terpene series, 1905- ; brucine and strychnine, 1910.

Thiele, J., Professor at Münich. Guanidine derivatives, 1902; tetrazole derivatives, 1895; nitramide, 1897; theory of "partial valencies," 1899; unsaturated lactones, 1902.

Von Pechmann, H. (1850-1803), Professor at Tübingen. On anthraquinone, 1880; coumarin-syntheses, 1883; α-diketones, 1887; *p*-xyloquinone from diacetyl, 1889; diazomethane, 1894; preparation of hydrazine, 1895.

Wallach, O., Professor at Göttingen. Extensive work in the terpene series, 1887- .

Willstätter, R., Professor at Münich. Tropic acid, tropine and atropine, 1895-1903; ecgonine and cocaine, 1897-1903; lecithin, 1904; *o*-quinones, pyrones, 1905; chlorophyll, 1907- .

Wislicenus, J. (1835-1902), Professor at Würzburg and Leipzig. On aldehyde-ammonia condensations, 1859; lactic acids, 1861-1873; oxyacids from cyanhydrins, 1862; ketonic and other organic ester syntheses, 1869-82; alkyl-acetoacetic esters, 1883; stereochemistry, "Die räumliche Anordnung der Atome," 1887; pentamethylene syntheses, 1895.

APPENDIX B

THE following table is a chronological summary of the chief events of chemical interest since the time of Boyle, classified as experimental facts, prevailing views or theories, or matter of more general interest, such as the foundation of new societies or laboratories, or fresh applications of chemistry to the arts. The dependence of modern theory on practical research, and the alternation between practical and mental activity in successive phases of the evolution of modern chemistry, may thus be readily seen, whilst at the same time a résumé of the foregoing chapters is afforded.

Date.	Experimental.	Theoretical.	General.
1660	Boyle's law discovered.	——	——
1661	Boyle discovered methyl alcohol.	——	Boyle's "Chemista Scepticus"; Boyle's definition of an element.
1663	——	——	Royal Society of London founded.
1665	——	——	"Philosophical Transactions of the Royal Society" first published.
1668	Mayow on calcination and respiration.	——	——
1699	——	——	"Mémoires de l'académie des Sciences" first published.
1736	Duhamel distinguished potash from soda.	——	India-rubber introduced into Europe.
1738	——	——	Clayton commenced coal-tar distillation.
1744	——	Rouelle's definition of a "salt".	——

Date.	Experimental.	Theoretical.	General.
1746	——	——	Roebuck: chamber process for sulphuric acid.
1747	Marggraf discovered sugar in beet-juice.	——	——
1750	Watson prepared pure platinum.	——	——
1754	Marggraf distinguished alumina from lime.	——	——
1755	Black on carbonic acid and alkalies.	——	——
1762	Black discovered latent heat.	——	——
1769	Scheele isolated *d*-tartaric acid.	——	Coke first manufactured.
1771	Scheele discovered fluorine.	——	——
1772	Scheele discovered manganese. Rutherford isolated nitrogen.	——	Lavoisier's note to the French Academy.
1773	Rouelle discovered urea.	——	——
1774	Scheele distinguished baryta from lime. Scheele discovered chlorine, oxygen and acetaldehyde. Priestley discovered oxygen.	——	——
1776	Scheele discovered oxalic and uric acids.	——	——
1777	——	Lavoisier's theory of combustion; Wenzel's law of mass-action.	——
1779	Scheele discovered glycerine.	——	Achard commenced beet-sugar manufacture.
1780	Scheele discovered pyromucic and lactic acids.	——	——
1782	Scheele discovered prussic acid. Cavendish showed that hydrogen burnt to form water.	——	——

1782	Guyton de Morveau obtained washing soda from Glauber's salt.	——	——
1783	Lavoisier: first quantitative synthesis of water. Lavoisier showed alcohol and carbon dioxide result from sugar fermentation.	——	Royal Society of Edinburgh founded.
1784	——	——	Cort introduced wrought-iron puddling process.
1785	Charles discovered law of expansion of gases. Scheele isolated malic acid.	——	——
1786	Scheele discovered pyrogallol.	——	——
1787	——	——	Lavoisier: classification of compounds.
1788	——	——	Le Blanc: soda process.
1789	——	——	"Annales de Chimie" first published.
1791	——	Richter: laws of neutralization of acids and bases.	——
1792	——	——	Murdoch introduced coal-gas.
1795	Preparation of ethylene.	——	École polytechnique, Paris, founded.
1796	Lampadius discovered carbon bisulphide.	——	——
1797	Vauquelin discovered chromium.	——	——
1799	Klaproth obtained mellitic acid. Welter discovered picric acid.	——	——
1800	Nicholson and Carlyle: quantitative electrolysis of water.	——	——
1801	——	——	——
1802	Wollaston on spectroscopy.	——	Proust-Berthollet controversy opened.
1803	Séguin prepared "morphium". Derosne isolated narcotine.	——	——
1804	——	——	——
1805	Northmore liquefied chlorine.	——	——

Date.	Experimental.	Theoretical.	General.
1805	Vauquelin discovered *l*-asparagine.	——	——
1806	——	Proust: law of constant combining proportions.	——
1807	Davy isolated sodium and potassium.	Dalton: law of multiple combining proportions; Dalton: law of partial pressures; Dalton's atomic theory; Davy's electrochemical theory.	——
1808	Davy isolated magnesium, calcium, barium.	Gay-Lussac's law of volumes.	——
1809	——	——	——
1810	Berzelius isolated silicon. Davy on elementary nature of chlorine. Wollaston discovered cystine.	——	Berzelius' "Jahresberichte" commenced.
1811	Gay-Lussac prepared anhydrous prussic acid. Courtois discovered iodine.	Avogadro's hypothesis.	Berzelius' system of chemical nomenclature.
1812	——	Berzelius' dualistic theory.	——
1813	——	——	——
1814	Fraunhofer on solar spectrum.	——	——
1815	Gay-Lussac's work on cyanogen begun. Biot on optical activity of sugar solutions.	Prout's hypothesis.	Vienna Polytechnic founded.
1816	——	——	——
1817	Arfvedson discovered lithium. Marcet discovered xanthine.	——	Chair of chemistry founded at Glasgow.

1817	Sertuerner discovered morphine.	——	——
1818	Pelletier and Caventou discovered strychnine. Prout prepared alloxan. Vauquelin discovered cyanuric acid.	——	——
1819	Garden isolated naphthalene. Liebig discovered fulminic acid. Pelletier and Caventou discovered brucine. Oersted discovered piperine.	Mitscherlich's law of isomorphism.	——
1820	Braconnot discovered glycocoll. Pelletier and Caventou discovered quinine and cinchonine.	——	Berlin Technical Institute founded.
1821	Pelletier discovered caffeine. Cagniard de la Tour on critical phenomena.	Dulong and Petit s law of specific heats; Mitscherlich on polymorphism.	——
1822	Kestner prepared *r*-tartaric acid.	——	——
1823	Braconnot discovered gun-cotton. Faraday on liquefaction of gases. Liebig and Wöhler on cyanic and fulminic acids.	——	——
1824	Gay-Lussac on volumetric analysis. Gmelin discovered taurine.	——	——
1825	Faraday discovered benzene and butylene.	——	Poggendorff's "Annalen" commenced.
1826	Balard discovered bromine. Unverdorben discovered aniline.	——	——
1827	Dumas' vapour density methods. Giesecke isolated coniine. Wöhler isolated aluminium.	——	——

Date.	Experimental.	Theoretical.	General.
1828	Wöhler transformed ammonium cyanate to urea. Posselt and Reimann discovered nicotine.	Dumas' etherin theory.	Neilson substituted hot for cold air in blast furnaces. University College, London, founded.
1829	——	Döbereiner's "triads" of elements.	King's College, London, founded.
1830	Dumas prepared oxamide. Robiquet discovered emulsin.	——	Liebig devised the modern combustion-furnace. Dumas' method for nitrogen estimation.
1831	Hesse discovered atropine. Liebig discovered chloroform. Leuchs discovered ptyalin.	——	Berzelius introduced the term isomerism. Ure used fulminates as detonators.
1832	Dumas and Laurent isolated anthracene. Liebig discovered chloral. Liebig and Wöhler on the radicle benzoyl. Liebig and Wöhler on the benzoin condensation. Serullas discovered iodoform.	Liebig's first radicle theory.	Liebig's "Annalen der Chemie" commenced.
1833	Graham on basicity of acids (phosphoric, arsenic, etc.). Mitscherlich discovered benzenesulphonic acid.	Faraday's laws of electrolysis.	——
1834	Chevreul discovered creatine. Dumas discovered substitution. Dumas and Péligot discovered cinnamic acid. Liebig on polybasic organic acids.	Berzelius-Mitscherlich contact theory of fermentation.	"Journal für praktische Chemie" first appeared.

1834	Runge discovered phenol and pyrrol in coal-tar. Mitscherlich prepared benzene and nitrobenzene from benzoic acid. Payen and Persoz discovered diastase.	——	——
1835	Laurent discovered anthraquinone. Schwann discovered pepsine.	——	"Comptes rendus de l'académie française" first published. Wöhler's laboratory at Göttingen erected. Liebig gave aldehydes their present name.
1836	E. Davy discovered acetylene. Cagniard de la Tour on growth of yeast during fermentation. Laurent obtained phthalic acid from naphthalene.	——	De la Rive introduced electroplating.
1837	Bunsen on the cacodyl radicle. Bouchardat discovered isoprene. Liebig and Wöhler discovered amygdalin.	Laurent's nucleus theory.	——
1838	Kane on mesitylene from acetone. Piria on salicylic acid.	Liebig's acetyl theory.	——
1839	——	Gerhardt's theory of residues; Liebig's vibration theory of fermentation.	Goodyear discovered vulcanization of rubber.
1840	Stas commenced his work on atomic weights.	Dumas' unitary type theory; Hess' laws of constant heat summation.	Bunsen's Marburg laboratory erected.
1841	Fritzsche prepared anthranilic acid.	——	Chemical Society founded.

Date.	Experimental.	Theoretical.	General.
1842	Kopp commenced his work on specific volumes. Zinin discovered α- and β-naphthylamines.	Liebig on nutrition.	——
1843	——	——	Laurent's defined atom, molecule, equivalent.
1844	Unger discovered guanine.	Gerhardt's homologous and isologous series.	Gerhardt and Laurent's classification and nomenclature of organic compounds.
1845	Gerhardt discovered sulphanilic acid. Gerhardt discovered the anilides. Hofmann discovered aniline in coal-tar. Kolbe on methylsulphonic acids. Regnault on gas densities.	Waterson on kinetic theory of gases.	College of Chemistry founded (merged into the Royal College of Science, 1890).
1846	Anderson isolated pyridine. Liebig discovered tyrosine. Faraday discovered magnetic rotation of polarized light.	——	——
1847	Dumas prepared acetamide. Liebig discovered sarcosine. Sobrero discovered nitroglycerine.	——	——
1848	Kolbe on electrolysis of fatty acid salts. Merck discovered papaverine.	——	"Journal of the Chemical Society" commenced.
1849	Fehling's test for sugars. Frankland on organo-metallic compounds. Wurtz prepared amines from cyanic esters.	——	——
1850	Hofmann prepared alkyl-amines and anilines.	——	——

1850	Scherer discovered inosite. Strecker discovered alanine. Wilhelmy on rate of inversion of cane-sugar.	— —	—
1851	Graham on diffusion. Pasteur commenced to study sodium ammonium tartrates.	— —	Laboratory erected at Owen's College, Manchester.
1852	Gerhardt prepared acid anhydrides. Williamson on preparation of ether.	—	—
1853	Frankland's work on valency commenced. Hittorf on transport numbers. Thomsen commenced thermo-chemical studies.	Gerhardt's four types. Williamson's mixed types.	—
1854	Williamson and Kay synthesized glycol.	— —	—
1855	Bunsen isolated lithium. Berthelot prepared isopropyl alcohol. Wurtz synthesized alkylparaffins.	Pasteur suggested that optical activity depended upon atomic asymmetry; Pasteur's vitalistic theory of fermentation.	—
1856	Perkin discovered mauveine.	—	Bessemer process for steel manufacture.
1857	Deville on dissociation.	Clausius' kinetic theory.	—
1858	Berthelot synthesized methyl alcohol. Fittig prepared pinacones. Perkin and Duppa on glycocoll.	Cannizzaro on atomic weight determination; Couper and Kekulé on quadrivalency of carbon; Gladstone-Dale formula for molecular refraction.	Société chimique de Paris founded.
1859	Neumann discovered cocaine. Wurtz prepared ethylene oxide.	Bunsen and Kirchhoff on spectroscopy.	Verguin manufactured rosaniline.

Date.	Experimental.	Theoretical.	General.
1860	Bunsen and Kirchhoff discovered rubidium and caesium by the spectroscope. Kolbe prepared salicylic acid from phenol.	——	——
1861	Berthelot and St. Gilles on esterification. Butlerow prepared methylenitan from trioxymethylene. Crookes discovered thallium. Strecker prepared guanidine.	——	Solvay: ammonia-soda process.
1862	Strecker discovered choline. Kolbe synthesized taurine. Graham on colloids.	——	Nobel introduced dynamite.
1863	Berthelot synthesized acetylene. Geuther prepared acetoacetic ester. Griess prepared the first diazo compounds. Fittig synthesized aromatic hydrocarbons. Schulze discovered α- and β- naphthols. Will discovered myronic acid.	——	——
1864	Brodie on acid peroxides. Butlerow on action of zinc alkyls with acid chlorides.	Newlands' law of octaves.	"Bulletin de la société chimique de Paris" first published.
1865	Berthelot commenced his researches on thermo-chemistry.	——	Crum Brown's structure notation.
1866	Baeyer obtained mesityl oxide and phorone from acetone.	——	——

1866	Hofmann prepared isonitriles. Hofmann synthesized guanidine.	——	——
1867	Lister used phenol as an antiseptic. v. Than discovered carbon oxysulphide.	Guldberg and Waage's law of mass action; Claus' "diagonal" benzene formula; Kekulé's benzene theory.	Caro introduced Bismarck brown. Deutsche Chemische Gesselschaft founded.
1868	Hofmann prepared formaldehyde. Hofmann prepared amines from isonitriles. Hofmann: vapour density determination. Perkins' synthesis of cinnamic acid. Wurtz's synthesis of choline.	——	Weldon: chlorine process. "Berichte der deutschen Chem. Gesselschaft" commenced to appear.
1869	Baeyer synthesized indol. Andrews on critical phenomena. Gräbe and Liebermann synthesized alizarin. Scheibler discovered betaïne. Volhard synthesized creatine.	L. Meyer on physical properties and atomic weights; Mendelejew's periodic system; Körner's pyridine formula; Ladenburg's "prism" benzene formula.	——
1870	Baeyer on mellitic acid. Berthelot synthesized benzene. Friedel and Crafts' synthesis of aromatic hydrocarbons. Liebig discovered invertase.	——	——
1871	Baeyer on orientation of benzene compounds. Gräbe and Caro synthesized acridine. Kekulé prepared triphenylmethane.	Dewar's quinoline formula.	——

Date.	Experimental.	Theoretical.	General.
1872	Griess on orientation of benzene derivatives. Kolbe on aliphatic nitro-compounds. Wurtz on aldol condensation.	——	Baeyer introduced fluorescein.
1873	Gräbe synthesized carbazole. Wislicenus on isomeric lactic acids.	——	——
1874	Baeyer and Caro on aromatic nitroso-compounds. Körner on orientation of benzene derivatives. Ladenburg on equivalence of hydrogen atoms in benzene.	Le Bel-Van 't Hoff's steric conception of an atom of carbon.	——
1875	E. Fischer prepared phenylhydrazine. Lassen prepared hydroxylamine. Perkin synthesized coumarin.	——	Winkler: contact process for sulphuric acid.
1876	——	——	American Chemical Society founded.
1877	Conrad on syntheses from malonic ester. Hofmann discovered quercite. E. Fischer prepared the first phenylhydrazone. Pfeffer on osmotic pressure. Pictet and Cailletet on liquefaction of gases. Wislicenus commenced studies of *cis-trans*-isomerism.	Butlerow on tautomerism; Blomstrand's diazonium formula for diazo-salts.	——
1878	V. Meyer's vapour density method. E. and O. Fischer on rosaniline.	Van 't Hoff's steric theory of nitrogen atom; Gibb's phase rule.	O. Fischer introduced malachite green.

1879	Fischer prepared alkylhydrazines. Remsen and Fahlberg prepared saccharin.	Nietzski's theory of colour.	"American Chemical Journal" first published.
1880	Baeyer synthesized isatin. V. Meyer discovered thiophene.	Lorenz and Lorentz's formula for molecular refraction; Zincke regarded sugars as aldehyde alcohols.	Deacon's chlorine process. "Monatschrift für Chemie" first appeared.
1881	Claisen condensation discovered.	Van der Waals' equation of condition.	Brin: oxygen process. Society of Chemical Industry founded.
1882	Baeyer synthesized indigo. V. Meyer prepared the first oxime. Rügheimer synthesized piperine.	——	Weldon-Péchiney: manganese recovery process (in chlorine manufacture).
1883	Baeyer synthesized alloxan. Curtius prepared diazoacetic ester. Erlenmeyer synthesized tyrosine. V. Meyer isolated two benzildioximes. Olzscewski and Wroblewski on liquefaction of gases.	——	Kjeldahl's method for estimation of nitrogen.
1884	Bischoff on syntheses from ketonic esters. E. Fischer prepared osazones from sugars.	Van 't Hoff's Études de dynamique chimique.	——
1885	Brieger discovered cadaverine. E. Fischer commenced synthetic work on sugars. Kiliani's method of sugar-synthesis. Kossel discovered adenine. Merck synthesized cocaïne.	Balmer's formula for hydrogen spectrum; Laar on tautomerism; relation of furfurane, thiophene, pyrrol, coumarone, indol, etc., to each other and to benzene recognized.	Welsbach introduced incandescent gas-mantles. Castner-Kellner electrolytic manufacture of caustic soda.

Date.	Experimental.	Theoretical.	General.
1886	Ladenburg synthesized coniine. Ladenburg synthesized ptomaines. Loew obtained formose from formaldehyde. Moissan isolated fluorine. Piutti discovered *d*-asparagine.	Crookes' protyle theory.	Vieille discovered a safe detonator for nitrocellulose.
1887	Baeyer commenced to work out the reduction products of benzene. E. Fischer prepared *α*-acrose (*dl*-fructose). Knorr prepared derivatives of pyrazole. Piutti and Korner synthesized asparagin.	Arrhenius' ionic theory.	"Zeitschrift für physikalische chemie" first appeared.
1888	Behrend and Roosen synthesized uric acid. Raoult on determination of molecular weight by depression of freezing-point.	Crookes' theory of meta-elements.	——
1889	Beckmann on determination of molecular weight by elevation of boiling-point.	——	——
1890	E. Fischer synthesized *d*-glucose. Lehmann on liquid crystals.	Bischoff's steric view of nitrogen atom; Crum Brown - Guye quantitative theory of optical activity; Hantzsch-Werner theory of isomeric oximes.	Castner: electrolytic manufacture of sodium.
1891	Le Bel resolved a compound containing asymmetric nitrogen.	Ostwald's classification of physical properties.	——

	rotatory power.	Armstrong-Baeyer "centric" benzene formula.	Baeyer's *cis-trans*-terminology. Moissan; manufacture of calcium carbide.
1893	Claisen on tribenzoylmethane tautomerism. E. Fischer on alkylglucosides. Fleck on magnesium ethide. Landolt commenced revision of the law of conservation of mass. Ramsay and Rayleigh discovered argon. Ramsay and Shields on surface tension. Wohl's method of sugar-synthesis.	——	Moissan: preparation of refractory elements and of carborundum by the electric furnace.
1894	Fittig commenced study of lactones and paraconic acids. V. Pechmann prepared diazomethane.	Hantzsch's diazo-theory; Knorr on tautomerism; V. Meyer on steric hindrance.	——
1895	Haller partially synthesized camphor. Kostanecki commenced syntheses of xanthone dyes. Ramsay discovered helium. Discovery of the "Walden inversion".	——	Hampson-Linde process for liquefaction of gases.
1896	Becquerel on radioactivity of uranium. Buchner on sugar fermentation without living cells. Hantzsch on phenylnitromethane and ψ-bases. Knorr on diacylsuccinic esters (tautomerism). Kossel discovered tryptophane.	——	Hargreaves-Bird electrolytic soda process.
1897	E. Fischer synthesized uric acid. Gattermann extended the Friedel-Crafts' reaction to preparation of aromatic ketones.	Collie's steric benzene formula; Kauffmann's theory of fluorescence.	——

Date.	Experimental.	Theoretical.	General.
1898	Dewar liquefied hydrogen. E. Fischer synthesized guanine and purine. Ramsay and Travers isolated neon, krypton, xenon. Ruff's method of sugar-synthesis.	Lapworth on mechanism of intramolecular change.	Goldschmidt thermite process.
1899	Barbier on magnesium and methyl iodide. Collie and Tickle discovered oxonium salts. E. Fischer discovered proline. E. Fischer synthesized caffeine. Marchlewski synthesized cane-sugar.	Thiele's theory of partial valency ; Thiele's formula for benzene.	——
1900	Gomberg on triphenylmethyl. Grignard's reagent discovered. E. Fischer commenced work on polypeptides. Loeb's electrolytic reduction of nitrobenzene. Smiles (and Pope and Peachey) resolved a compound containing asymmetric sulphur.	Guye and Friedrich on reduction of gas constants ; Hewitt's theory of fluorescence.	——
1901	E. Fischer synthesized proline. Marckwold and M'Kenzie's first asymmetric synthesis. Willstätter synthesized atropine. Traube synthesized uric acid, xanthine, caffeine, etc.	——	——

1902	Mme. Curie isolated radium salts. Pope and Neville resolved asymmetric selenium.	——	Readman and Parker: manufacture of phosphorus by electric furnace.
1903	E. F. Armstrong on constitution of polysaccharides. Bredig on colloids. Marckwald isolated polonium.	Lapworth's explanation of the benzoin condensation.	Birkeland and Eyde: nitrogen oxides from air. "Journal de chimie physique" commenced.
1904	Kipping's work on organic silicon derivatives commenced. A. Pictet synthesized nicotine.	Abegg's "normal" and "contra" - valencies; Lowry on dynamic isomerism.	——
1905	W. H. Perkin, jun., commenced synthesis of terpenes by aid of Grignard's reagent.	Baly and Desch on tautomeric change.	——
1906	Walden on ionising media.	Barlow-Pope theory of crystalline structure.	N. Caro: manufacture of barium cyanide or calcium cyanamides from alkalies and coal.
1907	Wilsmore and Stewart isolated keten. Willstätter and Veraguth isolated cyclo-octane. Zelinsky isolated cyclononane.	Cain's theory of diazo-compounds.	Collie's polyketide nomenclature.
1908	Kamerlingh Onnes liquefied helium.	Ramsay restated ionic theory in terms of the electron theory.	——
1909	A. Pictet synthesized papaverine. Willstätter obtained crystalline chlorophyll.	——	——

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